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A Study of the Equilibrium Diagrams of the Systems, Benzene-Toluene and Benzene-Ethylbenzene

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A STUDY OF
THE EQUILIBRIUM DIAGRAMS OF
THE SYSTEMS,
BENZENE-TOLUENE
AND
BENZENE-ETHYLBENZENE

By John B. Mullen

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VITA

The author was born in Chicago September 22, 1916, and has lived in Chicago throughout his life. He received his high school education at Loyola Academy, and his collegiate training at Loyola University of Chicago, from which he received the degree of Bachelor of Science in 1937. Since that time he has been engaged as Research Chemist with the Technical Service Bureau, Inc., of Chicago, and has been pursuing graduate studies in Chemistry at Loyola University.

INTRODUCTION

The purpose of this work is to study the equilibrium diagrams of the systems, benzene-toluene and benzene-ethylbenzene. The method employed is the investigation of cooling curves of binary mixtures of these substances. The equilibrium diagrams are then constructed from the data determined from the cooling curves.

I. REVIEW OF LITERATURE

A search of the literature reveals no information on the equilibrium diagrams of the systems benzene-toluene and benzene-ethylbenzene. Kramer (1) and Richiardi (2) have investigated the equilibrium diagrams of other binary systems of benzene and mono-substituted benzenes. The information contained in their papers is the only data available related to this problem.

Methods available for the investigation of equilibrium diagrams in general are given in standard works on the subject of the phase rule, such as those by Findlay (3) and Bowden (4). However, the published information on the technique required relates primarily to systems in which freezing points of the components and equilibium temperatures are not below room temperature, so that air can be used as cooling medium. Kramer and Richiardi, in the work previously cited, have developed methods for determining equilibrium temperatures in samples which solidify at low temperatures, using dry ice-acetone mixtures as coolant. In the present work, the same method was used in determining equilibrium temperatures within the range of the dry ice-acetone bath (the minimum temperature obtained with dry ice-acetone baths is about -78°C.).

II. APPARATUS AND ITS CALIBRATION

The apparatus used consisted of a cooling bath for lowering the temperature of the sample, and a thermocouple pyrometer system for determining the temperature of the sample as it is cooled.

For samples which begin to solidify above approximately -65°C., a cooling bath of acetone and dry ice was used. This cooling bath was contained in a beaker which was insulated with heavy layers of cotton to reduce rate of heat exchange with surroundings to a minimum. For samples which do not solidify within the range of dry ice-acetone mixtures, liquid air was used as coolant. Because of the necessity of protecting this substance from heat, it was contained in a Dewar flask.

To prevent excessively rapid cooling of the sample in the bath, the test tube containing the sample was placed in a larger tube before insertion into the bath. In practice it was found desirable to use an outer tube or jacket considerably larger than the sample tube, and to use rings of cork to hold the sample tube approximately centered in the jacket. A spiral of Nichrome wire was inserted into the sample, and agitated up and down during the test to keep the sample well mixed.

A copper-constantan thermocouple system was used, both thermocouple junctions being silver soldered. One thermocouple junction was placed in a reference constant-temperature bath, the other in the sample being cooled.

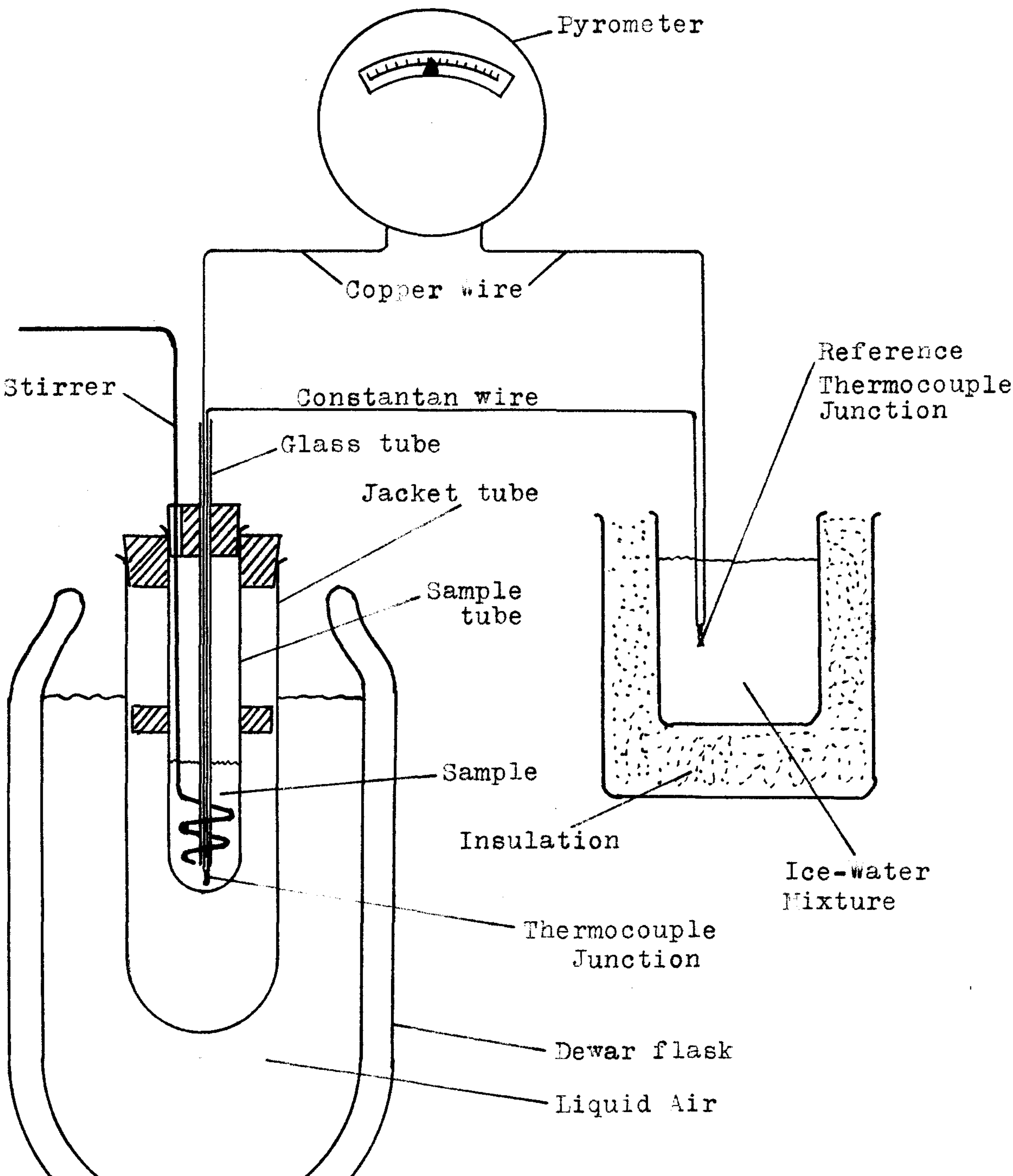


DIAGRAM OF APPARATUS

The electromotive force generated in the system was measured on a Brown Pyrometer, essentially a millivoltmeter with a range of 3.8 millivolts and an arbitrary scale of 100 units. Boiling tetrachloride, under reflux, was used as reference constant temperature bath in conjunction with the dry ice cooling bath, and a freezing mixture of ice and water was used in conjunction with the liquid air cooling bath.

The thermocouple pyrometer was calibrated by determining the freezing points, as indicated on the pyrometer scale, of various pure substances. Plotting the known freezing points of these substances, as ordinates, against the observed freezing points in scale units, as abscissae, gives a calibration curve by means of which any reading on the pyrometer can be translated into degrees centigrade. The materials used as calibration standards were carefully purified by distillation. The substances used in calibrating the pyrometer are given in the following table:

Substance	Freezing Point (Degrees Centigrade)
Benzene	5.5
Water	0.0
Carbon Tetrachloride	-22.6
Chloroform	-63.5
Toluene	-92.0
Ethyl Bromide	-117.8

In practice it was found that there were minor variations in the calibration of the instrument during the period of work. (A possible explanation of this lies in the fact that the thermocouple junctions had to be re-soldered at times, which both substituted a new junction and shortened the lead wires.) In addition, the temperature range of the instrument was intentionally shifted on more than one occasion. For these reasons, it was found desirable to calibrate the instrument before use every working period; and in the data presented in the following sections, calibration data and calibration curves will be found accompanying their respective cooling curve data and cooling curves.

III. PROCEDURE AND TECHNIQUE

To determine the solid-liquid equilibrium point of a mixture of given composition, it is necessary to run a "cooling curve" on the sample. In this procedure, a tube containing the mixture is placed in the cooling bath, with a stirring device to insure uniform temperature throughout the mixture during the test, and a thermocouple junction to measure the temperature of the mixture. The sample in the tube is then cooled and the temperature of the sample, as indicated on the thermocouple pyrometer, is recorded at intervals of 15 seconds. The sample is cooled until after the appearance of a solid phase. The temperature readings are then plotted, as ordinates, with time as abscissae, giving the cooling curve for the sample. The point at which the appearance of a solid phase began can be determined by inspection of the cooling curve. In the case of a pure substance, the rate of cooling (that is, the slope of the cooling curve) varies continuously and uniformly until solidification begins, at which point the temperature will remain constant until the solidification is complete. In the case of mixtures, there is a decrease in the rate of cooling when the solid phase first appears, caused by the evolution of the latent heat of fusion as the phase forms. This point can be observed as a pronounced "break" in the cooling curve, and the ordinate of that point represents the temperature at which a liquid of that composition is in equilibrium with solid. This is loosely spoken of as the "freezing point" of such a mixture.

If the components of the system are substantially immiscible in the solid state, and form no compounds, the solid phase which first appears will be one of the pure components, and it will appear, generally, at a temperature below the freezing point of the pure component. At a certain composition, the solid phase which separates out is a mixture of the two pure components, and the temperature at which this solid mixture forms is a constant for a given system. It is known as the eutectic point of the system, and is the lowest freezing point for any mixture within the system. It is the temperature at which both solid phases are in equilibrium with liquid. As a mixture of any composition within the system is cooled below the first appearance of solid, the pure solid component will continue to form and the liquid which is in equilibrium with the solid will become progressively poorer in that component until it reaches the eutectic composition and temperature. It will then solidify as the eutectic. The eutectic temperature can, therefore, be determined by continuing the cooling of any mixture within the system, below the appearance of the first solid phase, and until the temperature of the mixture remains constant. In practice, supercooling below the eutectic temperature frequently occurs, and the eutectic temperature is then indicated by a rise in the temperature of the mixture. In theory this should rise to the eutectic temperature, where it may or may not remain constant for an appreciable interval, but if the supercooling is considerable the latent heat evolved in solidification of the eutectic may not be sufficient to raise the temperature to the eutectic point.

If the equilibrium points for a series of such binary mixtures are plotted as ordinates, against composition as abscissae, the graph thus formed is known as the "equilibrium diagram" of the system, or commonly as the "phase diagram". It indicates what phases compose the system at equilibrium under any given conditions of temperature and for any composition.

In this work, binary mixtures were prepared by weighing the desired quantity of toluene or ethylbenzene (the less volatile component in either system) into a tared weighing bottle, the quantity of liquid being roughly measured from a graduated pipette. The desired quantity of benzene was then added, and the weight again determined. The weighing bottle was covered except during actual additions of either component. A portion of the sample was then transferred to the sample tube for cooling, placed in the cooling bath with the thermocouple junction and stirrer, and the cooling curve determined. All samples were prepared immediately before use to minimize evaporation losses.

In running the cooling curves, several precautions were found necessary. First, stirring of the mixture must be vigorous and continuous in order to avoid thermal gradients in the sample, so that the thermocouple pyrometer will truly represent the temperature throughout the sample at all times. Second, the pyrometer must be lightly tapped to overcome the inertia of the moving system and prevent sticking of the needle. On the other hand, excessive jarring disturbs the calibration of the instrument.

IV. OBSERVATIONS ON THE SYSTEM, BENZENE-TOLUENE

The following series of tables and graphs present the observations made on the benzene-toluene system. Table IV-1 gives the compositions of the mixtures prepared in this system. Tables IV-2 and following present the calibration data for the thermocouple pyrometer, and the pyrometer readings for each group of samples. These data are plotted in the group of illustrations which follow.

TABLE IV - 1

COMPOSITION OF SAMPLES, BENZENE-TOLUENE SYSTEM

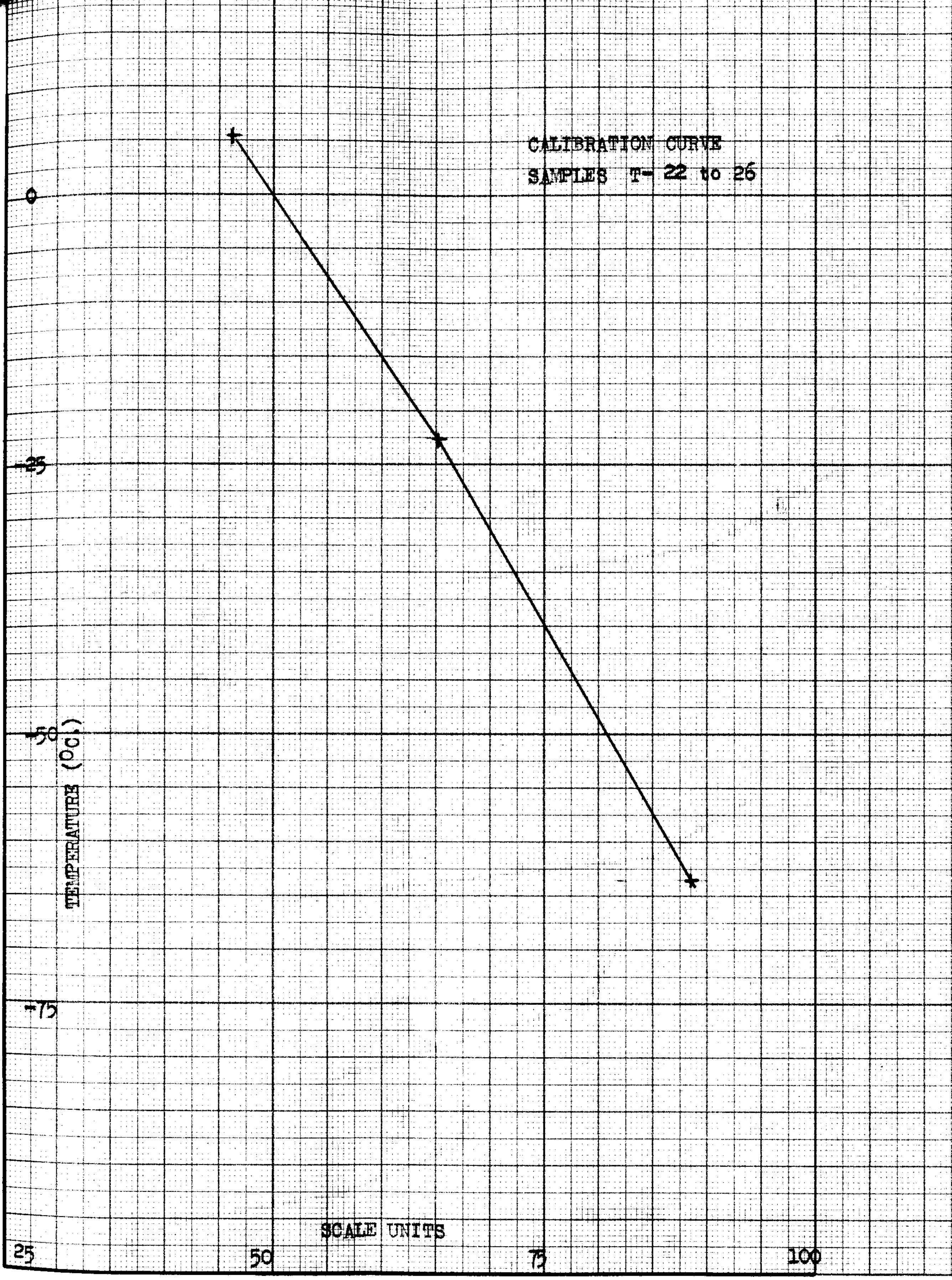
Sample	Weight of Toluene	Weight of Benzene	Total Weight	Percent Toluene	Percent Benzene
T-22	0.3831 g	7.5701 g	7.9532 g	4.819	95.196
T-23	0.8571	7.9238	8.7809	9.761	90.232
T-25	1.3476	7.3051	8.6527	15.574	84.424
T-26	1.7778	7.2183	8.9961	19.761	80.238
T-27	2.1730	6.4939	8.6669	25.07	74.93
T-28	2.7699	6.0421	8.8120	31.43	68.57
T-29	3.0981	5.6928	8.7909	35.24	64.76
T-30	3.3589	5.3397	8.6986	38.61	61.39
T-31	3.8351	4.8892	8.7243	43.96	56.04
T-32	4.5016	4.3982	8.8998	50.58	49.42
T-33	4.7658	3.9384	8.7042	54.75	45.25
T-34	5.1824	3.7425	8.9249	58.07	41.93
T-35	5.5865	3.1574	8.7439	63.89	36.11
T-36	6.0217	2.6272	8.6489	69.62	30.38
T-37	6.5565	2.3611	8.9176	73.52	26.48
T-38	7.0686	1.9833	9.0519	78.09	21.91
T-41	7.4381	1.3522	8.7903	84.62	15.38
T-42	7.8681	0.7679	8.6360	91.11	8.89
T-43	8.2624	0.3742	8.6366	95.67	4.33
T-44	6.9750	1,8969	8.8719	78.62	21.38
T-45	7.0067	1.7153	8.7220	80.31	19.67
T-46	7.5204	1.0951	8.6155	87.39	12.71

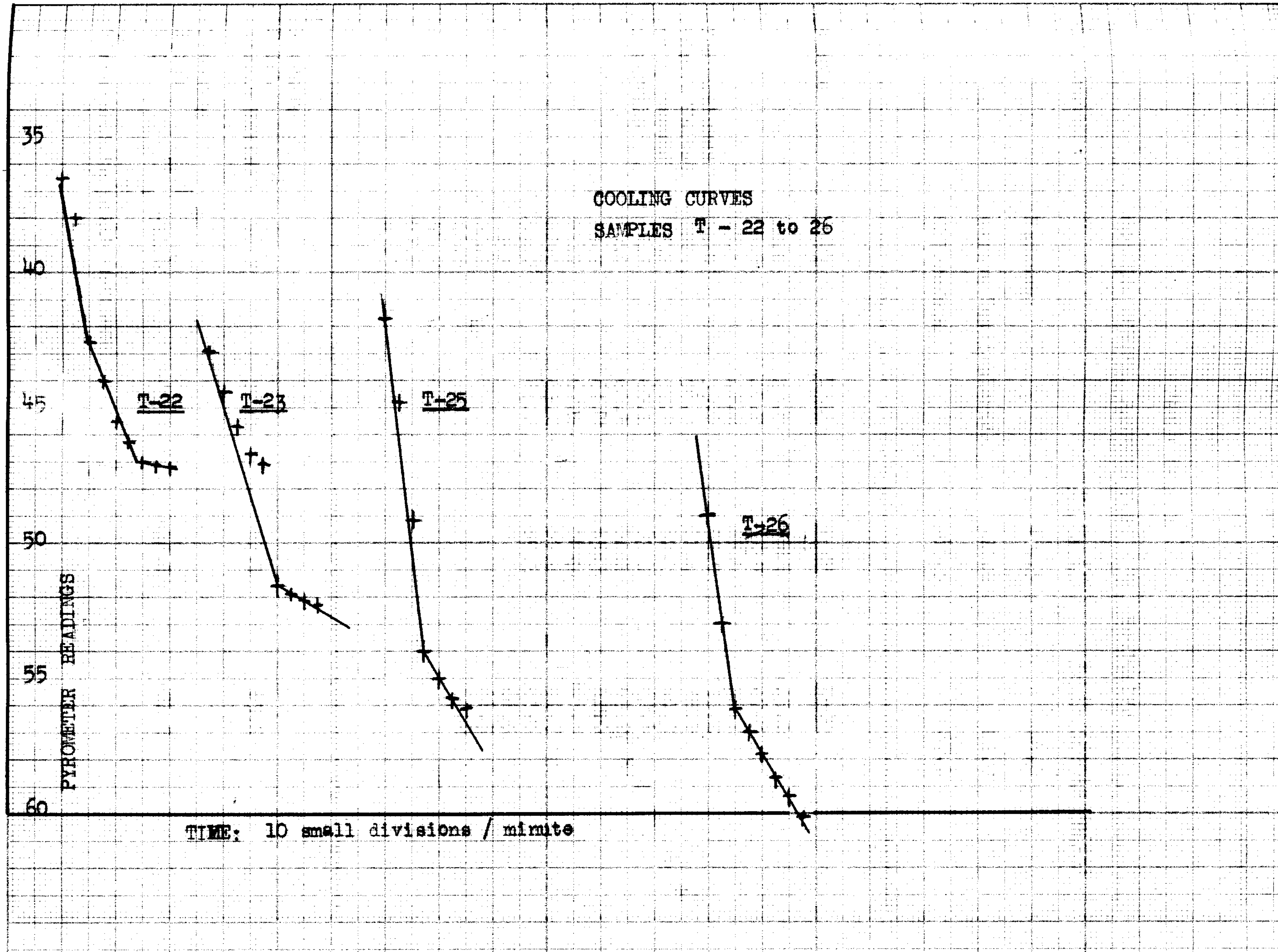
TABLE IV - 2

COOLING CURVES, SAMPLES T-22, 23, 25, and 26, inclusive

Calibration:	F. P. (°C)	F.P. (Scale Units)
Benzene	+ 5.5	46.2
Carbon Tetrachloride	-22.6	65.1
Chloroform	-63.5	88.5

Sample	T-22	T-23	T-25	T-26
Temperatures (Scale Units) at 15 second intervals.	36.5	36.2	41.7	49.0
	38.0	37.0	44.8	53.0
	42.5	37.9	49.2	56.2
	44.0	43.0	54.0	57.0
	45.5	44.4	55.0	57.8
	46.3	45.7	55.7	58.7
	47.0	46.7	56.2	59.4
	47.1	47.1		60.2
	47.2	51.6		
		51.9		
		52.1		
		52.3		
Freezing Point (Scale Units)	47.0	51.6	54.0	56.2
Freezing Point (°C)	4.2	- 2.5	- 6.1	- 9.5


CALIBRATION CURVE
SAMPLES T- 22 to 26
0
-25
-50
-75
TEMPERATURE (°C.)
SCALE UNITS
25
50
75
100



COOLING CURVES
SAMPLES T - 22 to 26
35
40
45
50
55
60
T-22
T-23
T-25
T-26
PYROMETER READINGS
TIME: 10 small divisions / minute

TABLE IV - 3

COOLING CURVES, SAMPLES T-27 - 35, inclusive

Calibration:		F. P. (°C)	F. P. (Scale Units)
	Benzene	+ 5.5	46.0
	Carbon Tetrachloride	-22.6	63.8
	Chloroform	-63.5	87.0

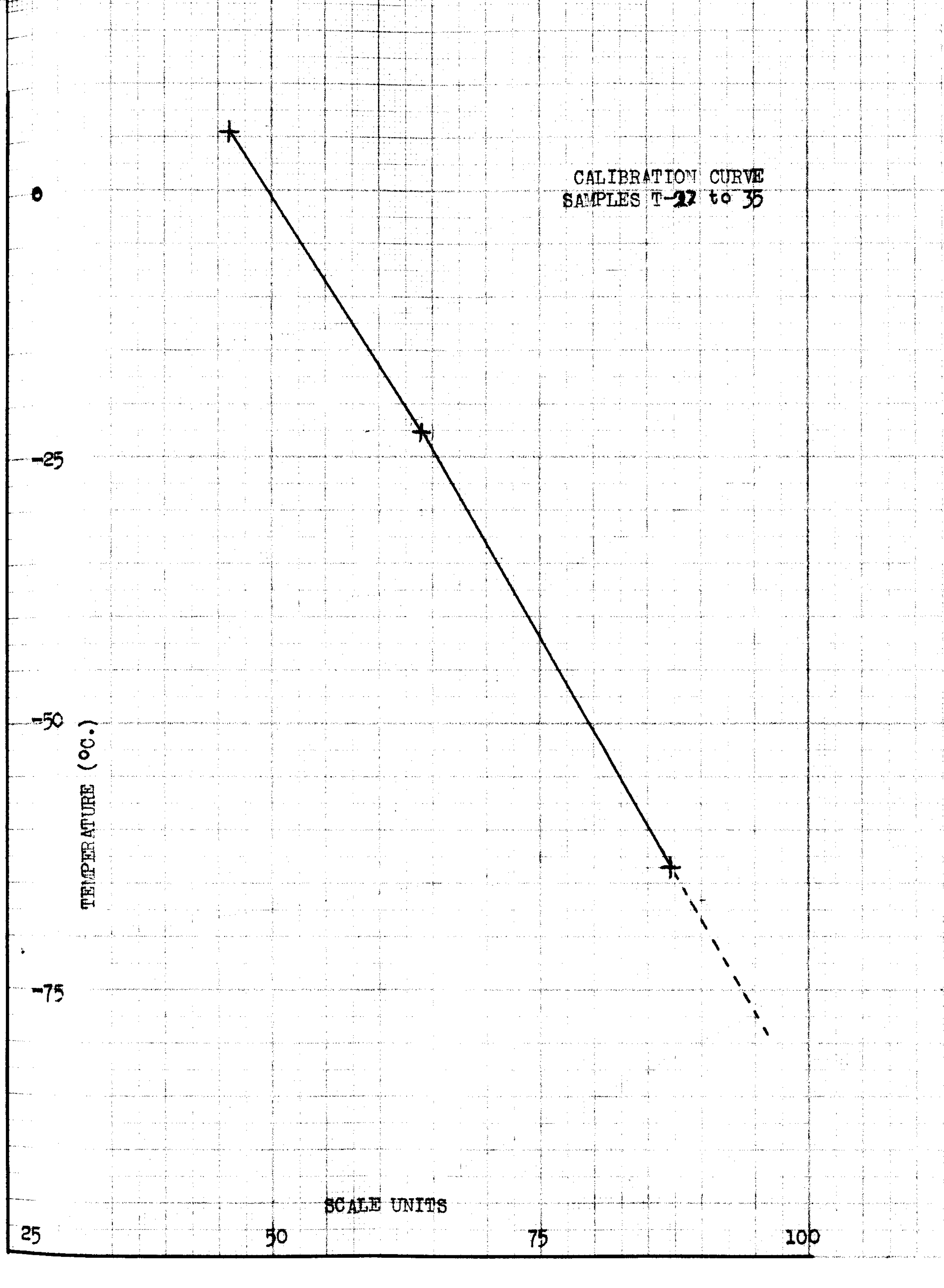
Sample	T-27	T-28	T-29	T-30
Temperatures (Scale Units) at 15 second intervals	42.0	43.0	46.8	45.2
	45.3	45.2	51.0	47.3
	47.5	47.2	55.6	52.7
	54.0	53.0	58.9	55.2
	56.7	56.0	61.4	58.0
	57.2	58.9	62.1	60.3
	58.2	60.1	63.1	62.6
	59.2	60.7	64.1	63.2#
	60.3	61.7	65.3	64.0
	61.7	62.4	66.7	63.8
	62.4	63.2	67.8	64.7
	63.2	64.2	69.3	65.6
	64.1			66.5
	64.8			66.5
	66.0			68.2
	66.9			
	67.8			
	69.3			
Freezing Point (Scale Units)	56.7	59.3	61.1	63.2
Freezing Point (°C)	-11.2	-15.3	-18.1	-21.3

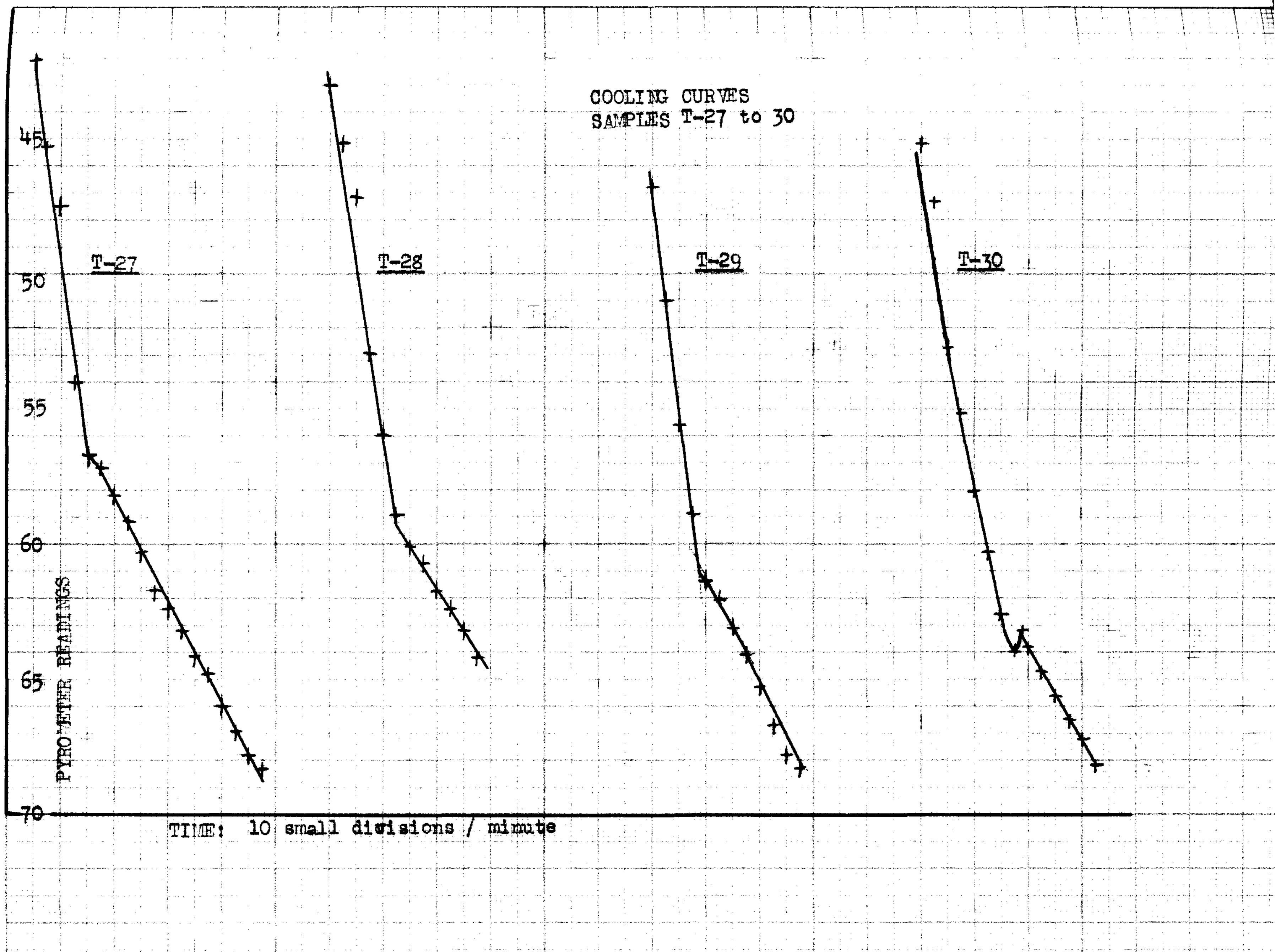
#Intermediate point (maximum)

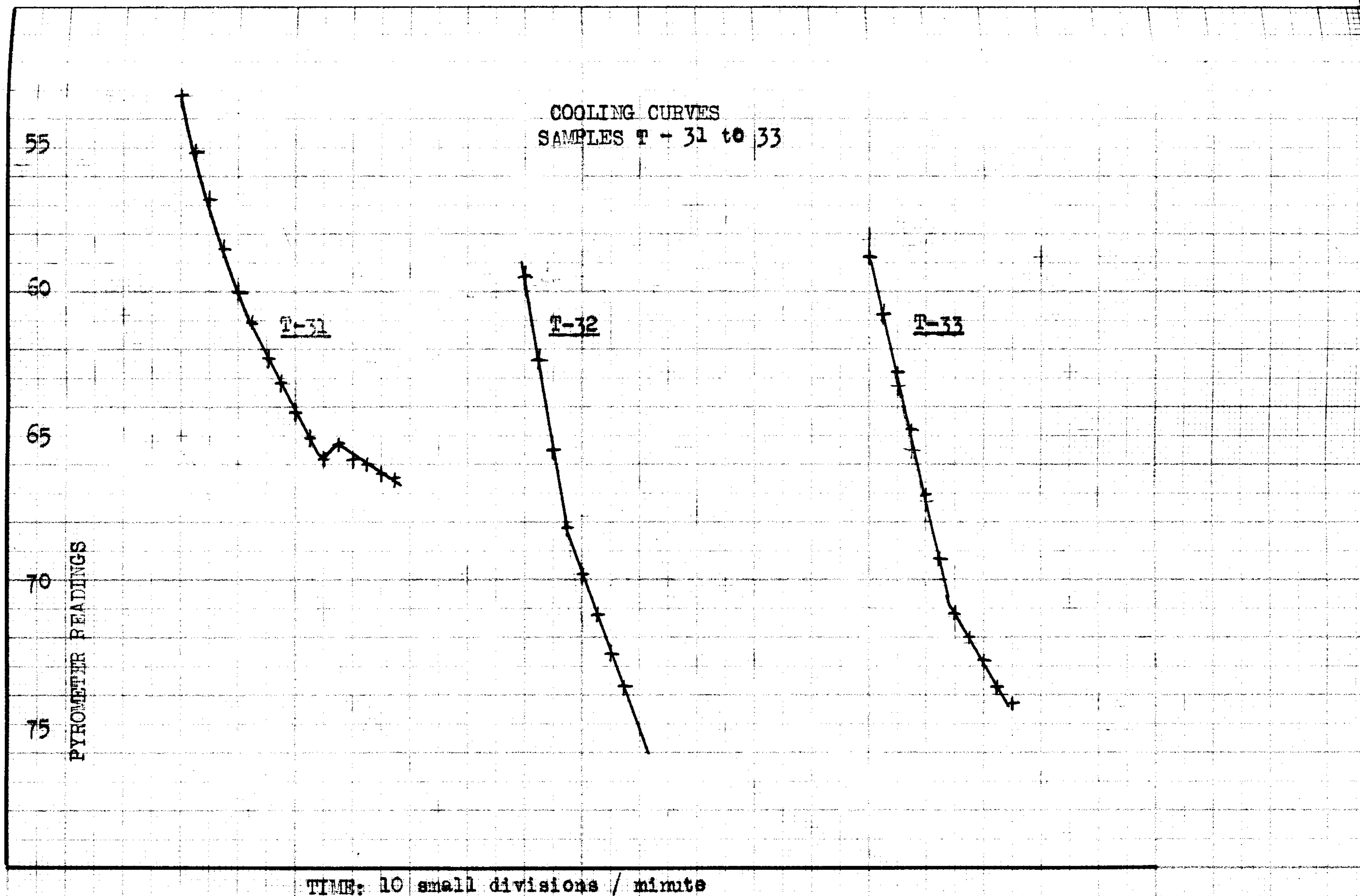
TABLE IV -3
(Continued)

Sample	T-31	T-32	T-33	T-34	T-35
	53.2	59.5	58.8	55.8	54.5
	55.2	62.4	60.8	59.1	58.2
	56.8	65.5	62.8	62.0	60.8
	58.5	68.2	64.8	64.5	63.3
Temperatures	60.0	69.8	67.1	66.8	65.8
(Scale Units)	61.1	71.2	69.3	69.0	68.0
at 15 second	62.3	72.5	71.2	71.0	69.9
intervals	63.2	73.7	72.0	72.7	71.3
	64.2		72.8	74.2	73.0
	65.1		73.7	75.2	74.0
	65.8		74.3	74.9#	75.2
	65.3			75.2	76.2
	65.8			75.8	77.0
	66.0			76.4	77.7
	66.3			77.2	78.1
	66.5			77.9	78.1
					78.5
					78.8
					78.9
					79.1
					79.4
					79.7
Freezing Point (Scale Units)	65.3	68.3	70.8	74.4	78.1
Freezing Point (°C)	-25.0	-30.1	-34.5	-41.0	-47.6

#Intermediate point (maximum)


CALIBRATION CURVE
SAMPLES T-27 to 35
0
-25
-50
-75
TEMPERATURE (°C.)
SCALE UNITS
25
50
75
100


COOLING CURVES
SAMPLES T-27 to 30
T-27
T-28
T-29
T-30
45
50
55
60
65
70
PYROMETER READINGS
TIME: 10 small divisions / minute



COOLING CURVES
SAMPLES T - 31 to 33
55
60
65
70
75
PYROMETER READINGS
T-31
T-32
T-33
TIME: 10 small divisions / minute

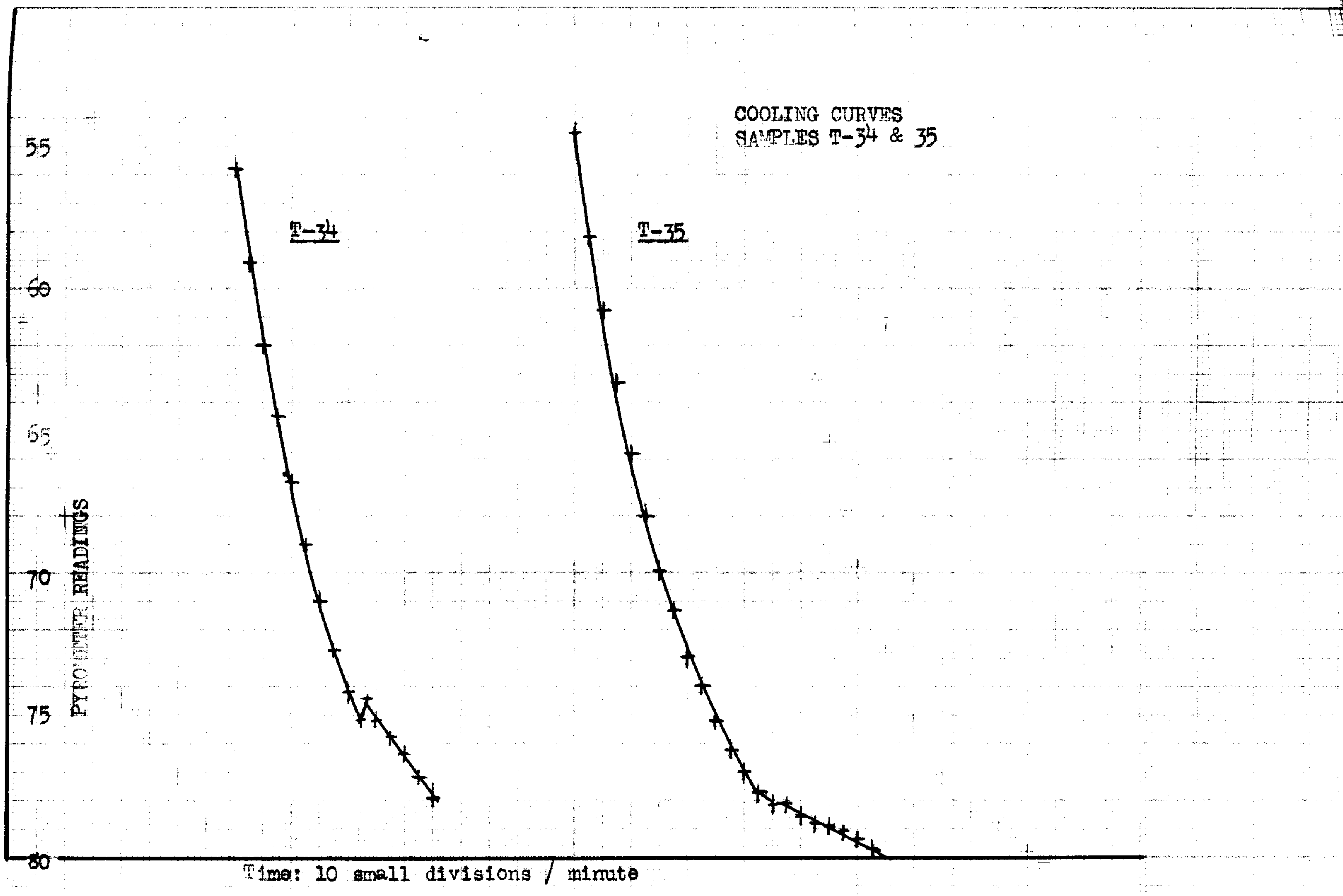
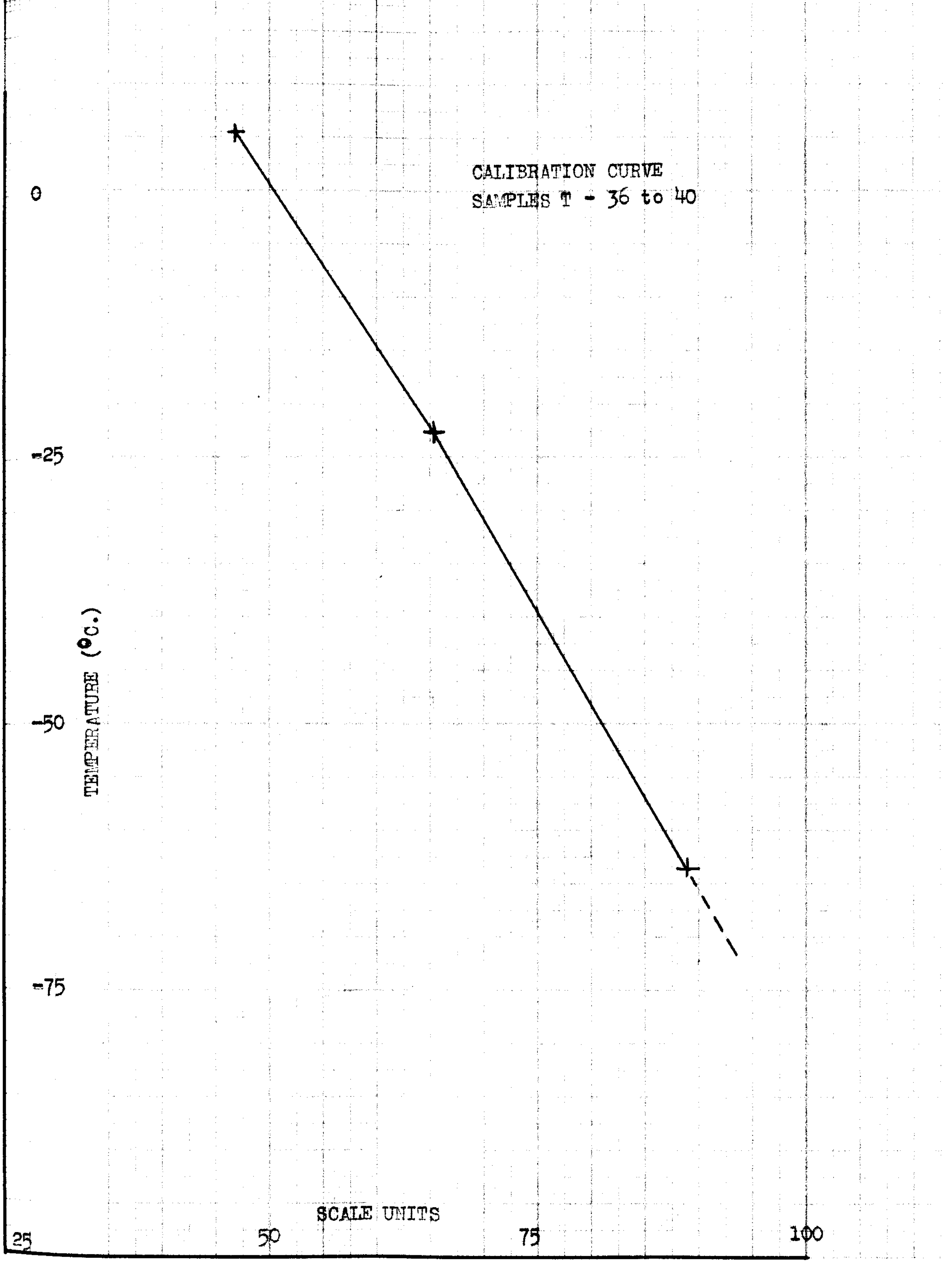

COOLING CURVES
SAMPLES T-34 & 35
T-34
T-35
PYROMETER READINGS
55
60
65
70
75
80
Time: 10 small divisions / minute

TABLE IV - 4
COOLING CURVES, SAMPLES T-36 - 38, inclusive

Calibration:		F. P. (°C)	F. P. (Scale Units)
	Benzene	+ 5.5	46.7
	Carbon Tetrachloride	-22.6	65.3
	Chloroform	-63.5	89.0

Sample	T-36	T-37	T-38
Temperatures (Scale Units) at 15 second intervals	68.8	67.2	79.8
	71.2	69.7	81.3
	74.0	72.5	83.0
	76.0	74.7	84.2
	77.8	76.5	85.2
	79.2	78.2	86.3
	80.7	80.0	87.2
	82.0	81.7	88.1
	83.7	82.9	88.8
	84.5	84.0	89.3
	85.7	85.1	90.0
	86.0	86.0	90.3
	86.3	86.8	90.7
	86.6	87.7	91.2
	86.9	88.2	91.6
	87.2	88.8	91.9
		89.0	92.2
		89.2	92.4
		89.7	92.6
		90.0	92.8
			93.0
			93.0
			93.0
			93.0
			93.0
			93.0
Freezing Point (Scale Units)	85.7	88.8	93.0
Freezing Point (°C)	-58.1	-63.4	-70.8


CALIBRATION CURVE
SAMPLES T - 36 to 40
TEMPERATURE (°C.)
0
-25
-50
-75
SCALE UNITS
25
50
75
100

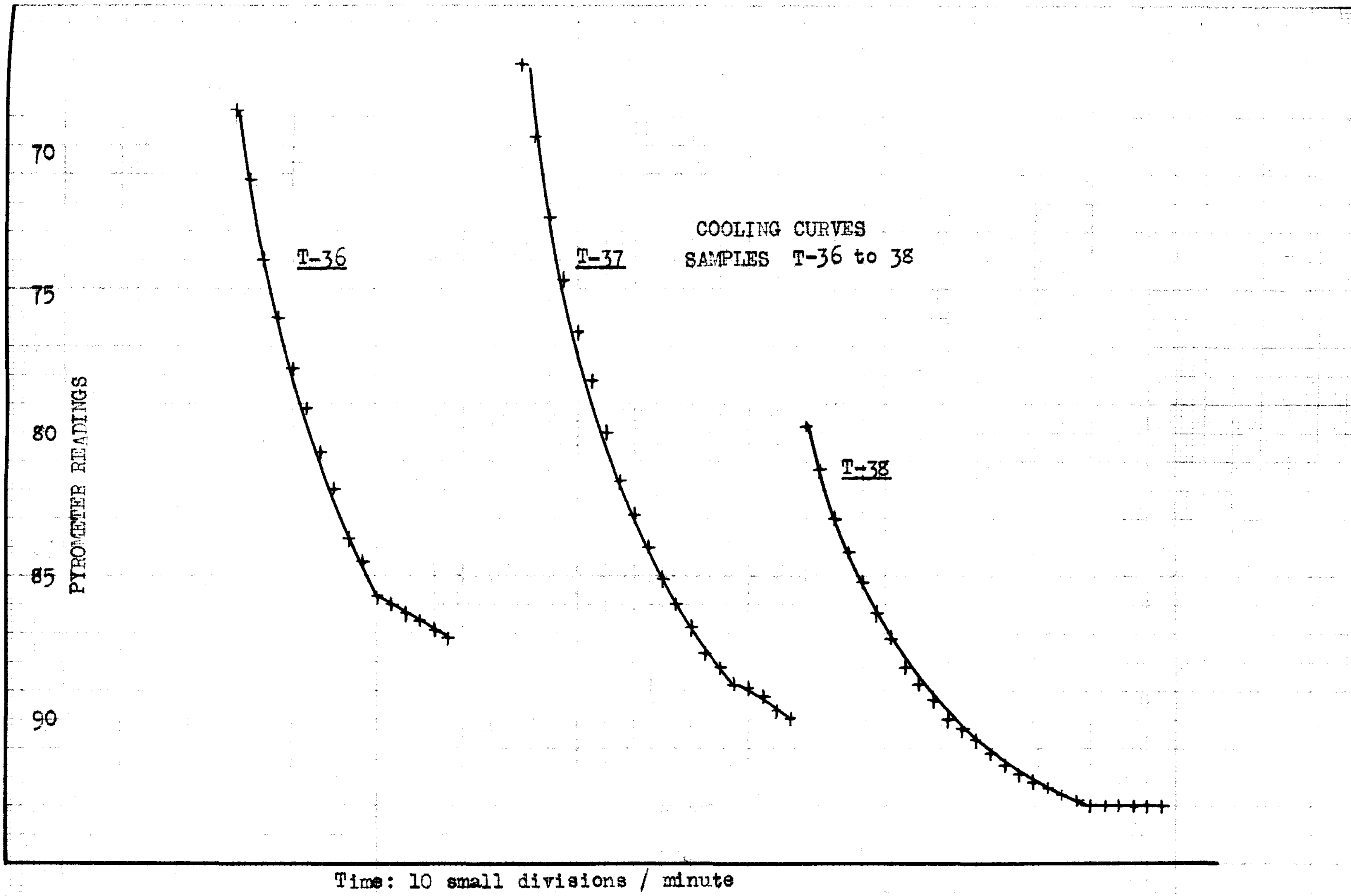
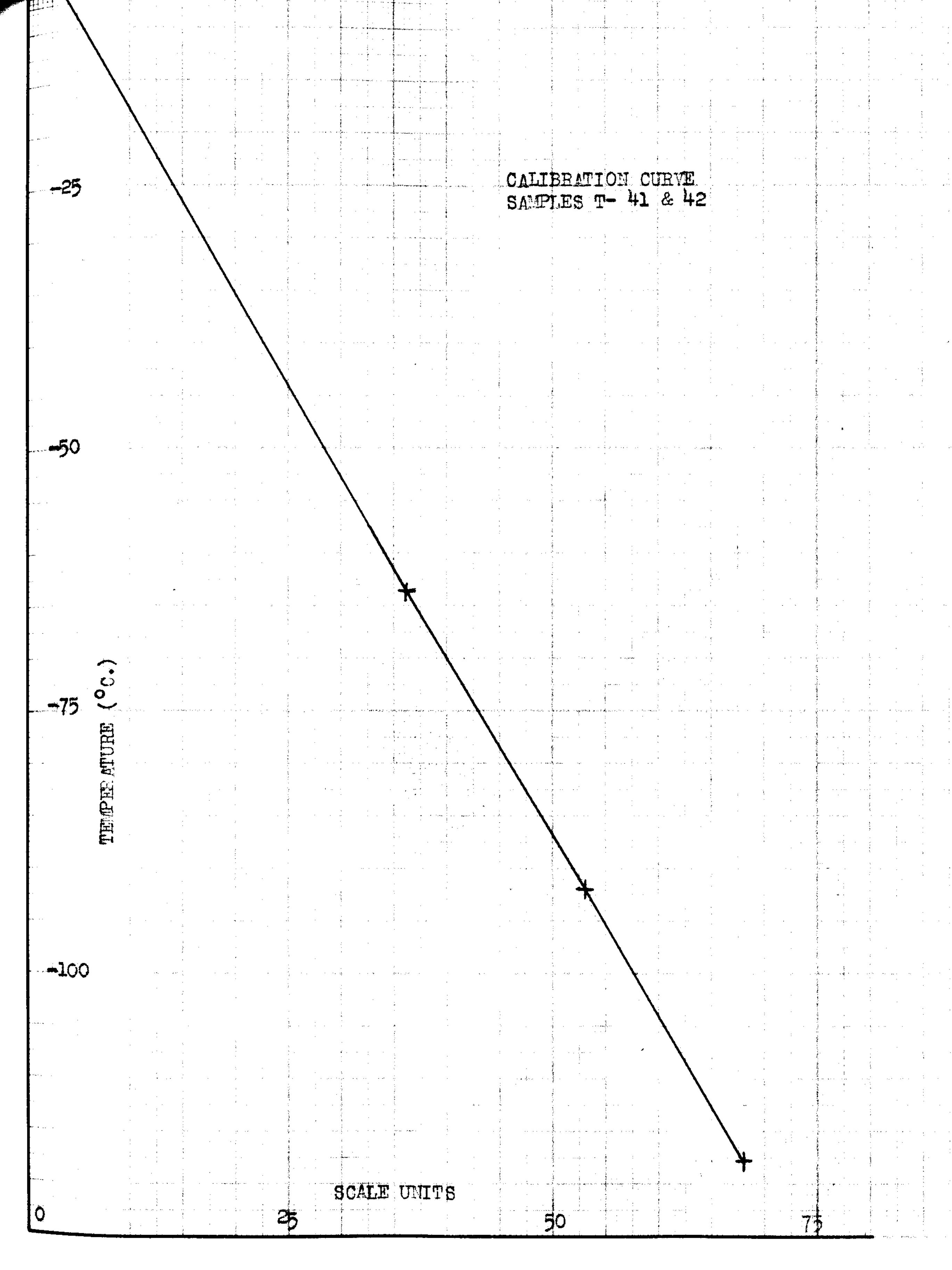

COOLING CURVES
SAMPLES T-36 to 38
T-36
T-37
T-38
70
75
80
85
90
PYROMETER READINGS
Time: 10 small divisions / minute

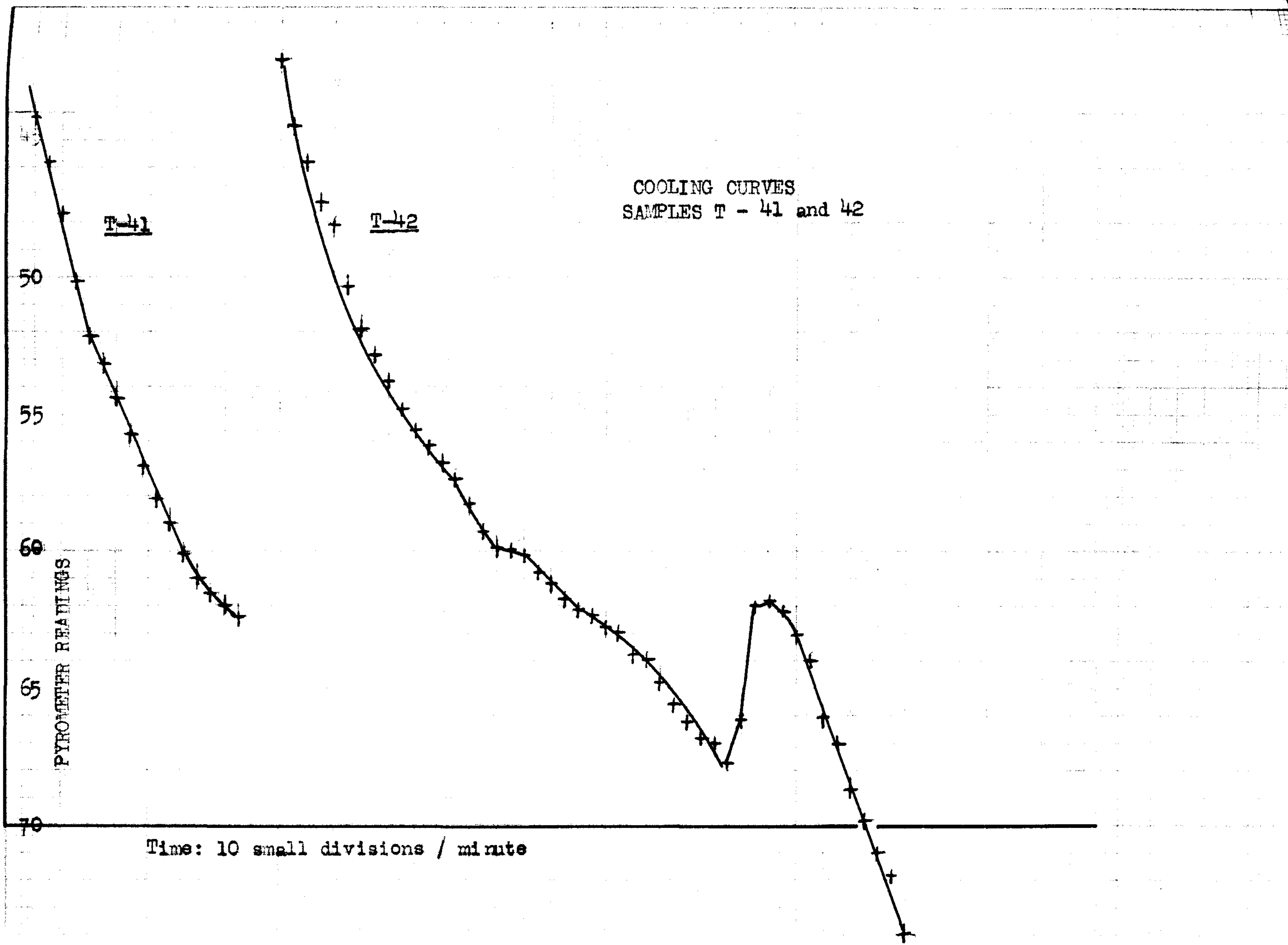
TABLE IV -5

COOLING CURVES, SAMPLES T-41, 42

Calibration:	F. P. (^{o}C)	F. P. (Scale Units)
Water	0.0	0.0
Chloroform	-63.5	36.2
Toluene	-92.0	53.3
Ethyl Bromide	-117.8	68.0

Sample	T-41	T-42		
	44.2	42.0	59.9	67.0
	45.8	44.5	60.0	67.2
	47.7	45.8	60.2	66.2
	50.2	47.3	60.8	62.0
Temperatures (Scale Units) at 15 second intervals	52.2	48.1	61.2	61.8
	53.2	50.4	61.8	62.2
	54.4	51.9	62.2	63.1
	55.8	52.8	62.3	64.0
	56.9	53.8	62.8	66.1
	58.1	54.8	63.0	67.0
	59.0	55.6	63.8	68.7
	60.1	56.2	64.0	69.8
	61.0	56.8	64.8	71.0
	61.6	57.4	65.6	71.8
	62.0	58.3	66.2	74.0
	62.4	59.3	66.8	
Freezing Point (Scale Units	52.2			59.9
Freezing Point (^{o}C)	-90.5			-104.0
Eutectic Temp. (Sclae Units)	-			61.8
Eutectic Temp. (^{o}C)	-			-107.2


CALIBRATION CURVE
SAMPLES T- 41 & 42
TEMPERATURE (°C.)
-25
-50
-75
-100
SCALE UNITS
0
25
50
75



COOLING CURVES
SAMPLES T - 41 and 42
T-41
T-42
PYROMETER READINGS
50
55
60
65
70
Time: 10 small divisions / minute

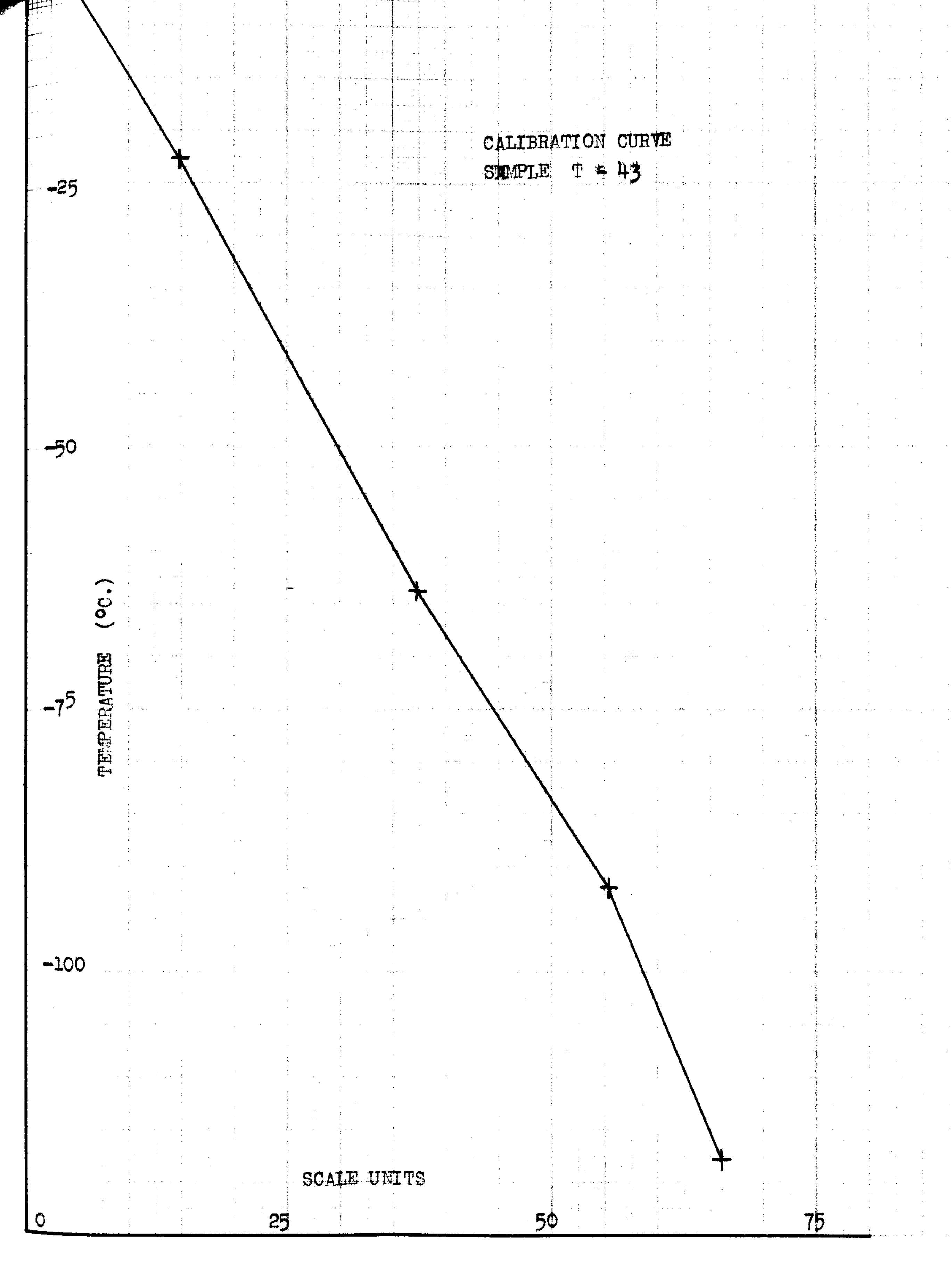
TABLE IV - 6

COOLING CURVES, SAMPLE T-43

Calibration:	F. P. (°C)	F. P. (Scale Units)
Water	0.0	1.0
Carbon Tetrachloride	-22.6	14.8
Chloroform	-63.5	37.2
Toluene	-92.0	55.2
Ethyl Bromide	-117.8	66.0

Sample	T-43
Temperatures (Scale Units) at 15 second intervals	51.8
	53.0
	54.1
	55.2
	56.3
	57.2
	58.1
	59.0
	59.8
	60.2
	56.7
	56.1
	56.2
	56.2
	56.3
	56.6
	56.9
	57.2
	58.0
	58.8
	60.0
	61.2
	63.0

Freezing Point (Scale Units)	56.1	Freezing Point (°C)	-94.0


CALIBRATION CURVE
SAMPLE T - 43
-25
-50
-75
-100
TEMPERATURE (°C.)
SCALE UNITS
0
25
50
75

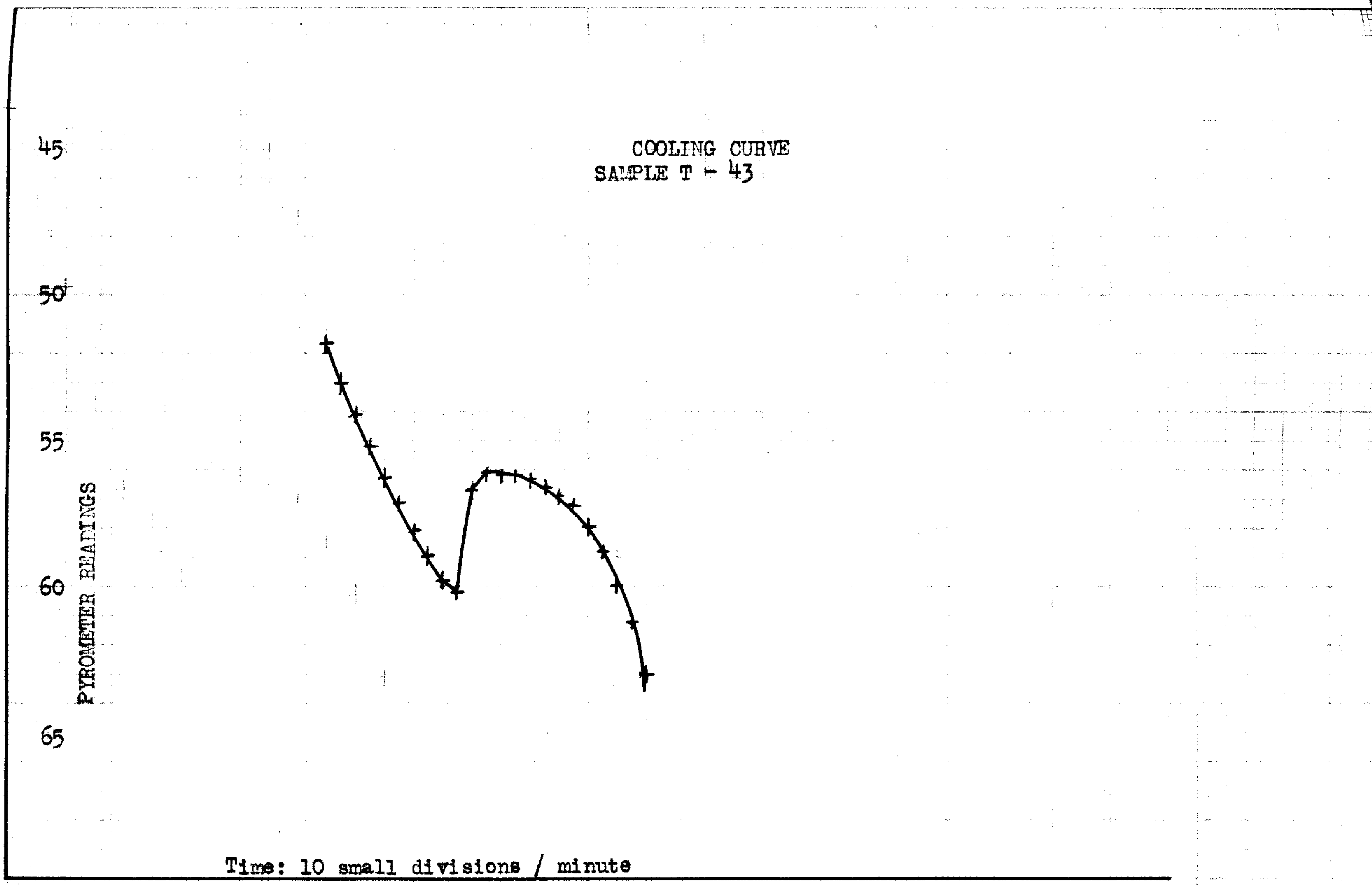
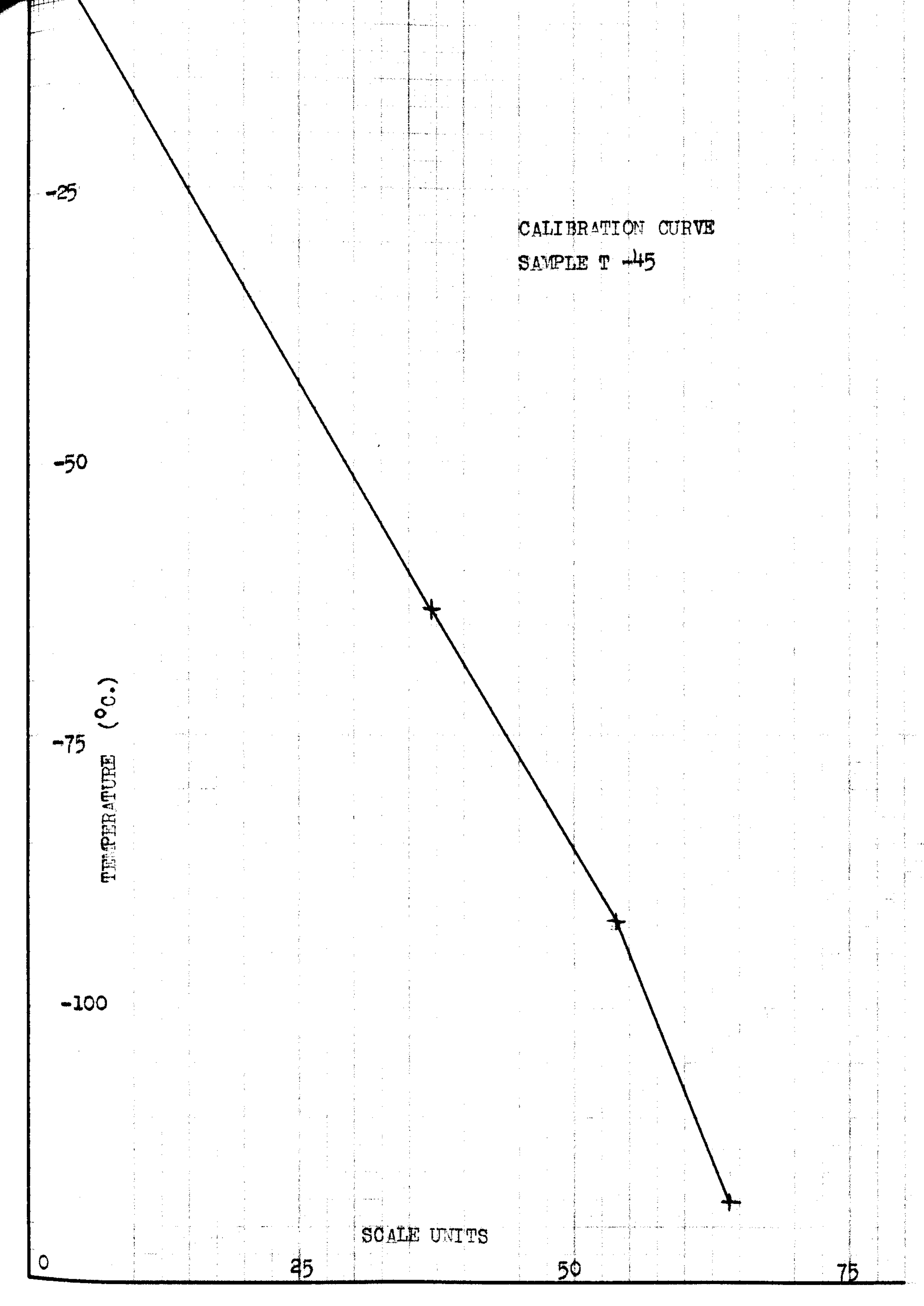
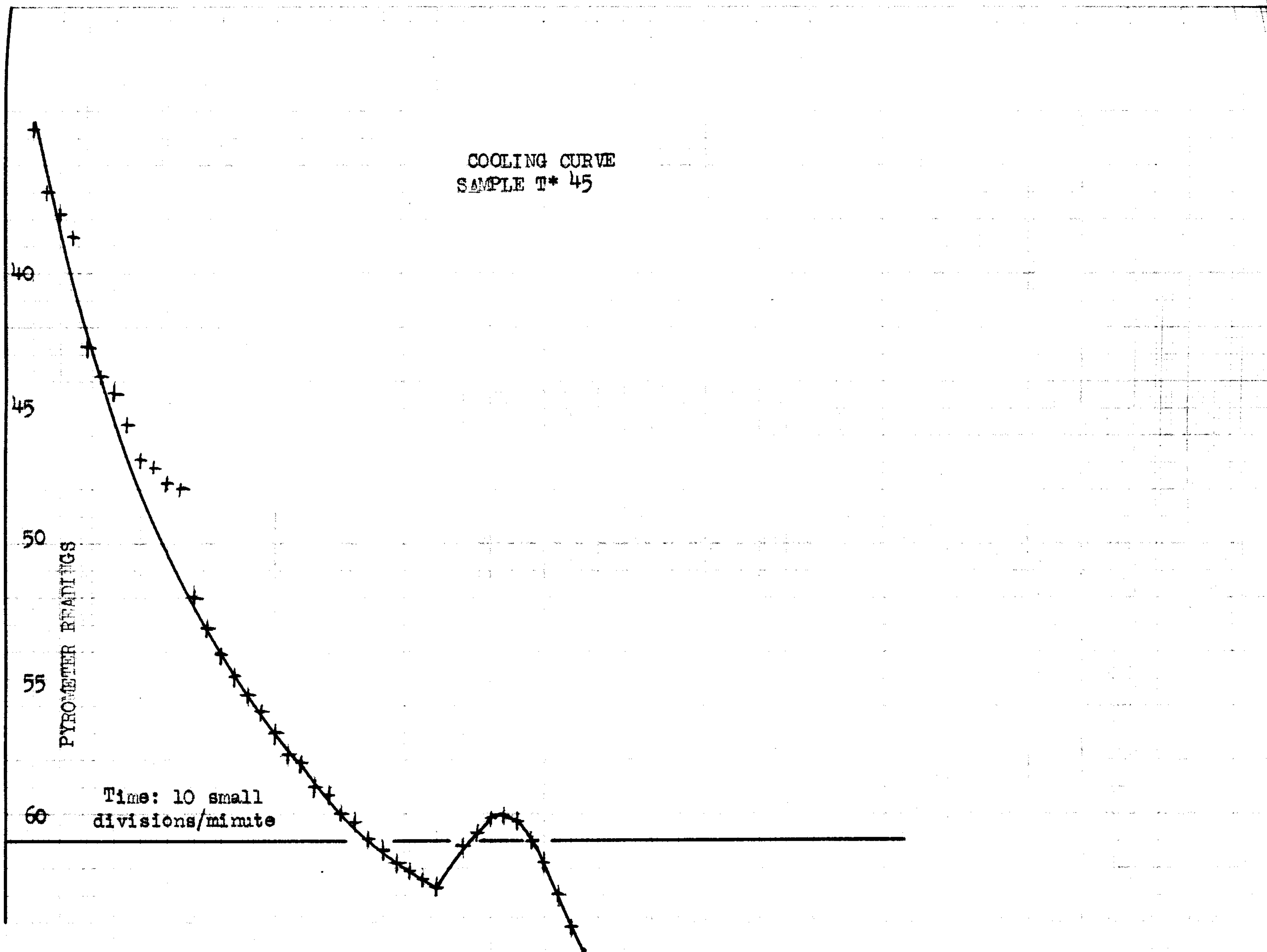

COOLING CURVE
SAMPLE T - 43
45
50
55
60
65
PYROMETER READINGS
Time: 10 small divisions / minute

TABLE IV- 7
COOLING CURVE, SAMPLE T-45

Calibration:		F. P. (°C)	F. P. (Scale Units)
	Water	0.0	0.2
	Chloroform	-63.5	37.0
	Toluene	-92.0	53.8
	Ethyl Bromide	-117.8	64.2

Sample	T-45	
Temperatures (Scale Units) at 15 second intervals	34.7	59.0
	37.0	59.3
	37.8	60.0
	38.6	60.3
	42.7	60.9
	43.8	61.3
	44.4	61.8
	45.6	62.1
	46.9	62.4
	47.2	62.7
	47.8	-
	48.0	61.2
	52.0	60.7
	53.1	60.2
	54.1	60.1
	54.9	60.3
	55.6	61.0
	56.2	61.8
	57.0	63.0
	57.8	64.2
	58.1	65.3
Eutectic Temp. (Scale Units)		60.1
Eutectic Temp. (°C)		-107.7


CALIBRATION CURVE
SAMPLE T -45
TEMPERATURE (°C.)
-25
-50
-75
-100
SCALE UNITS
0
25
50
75

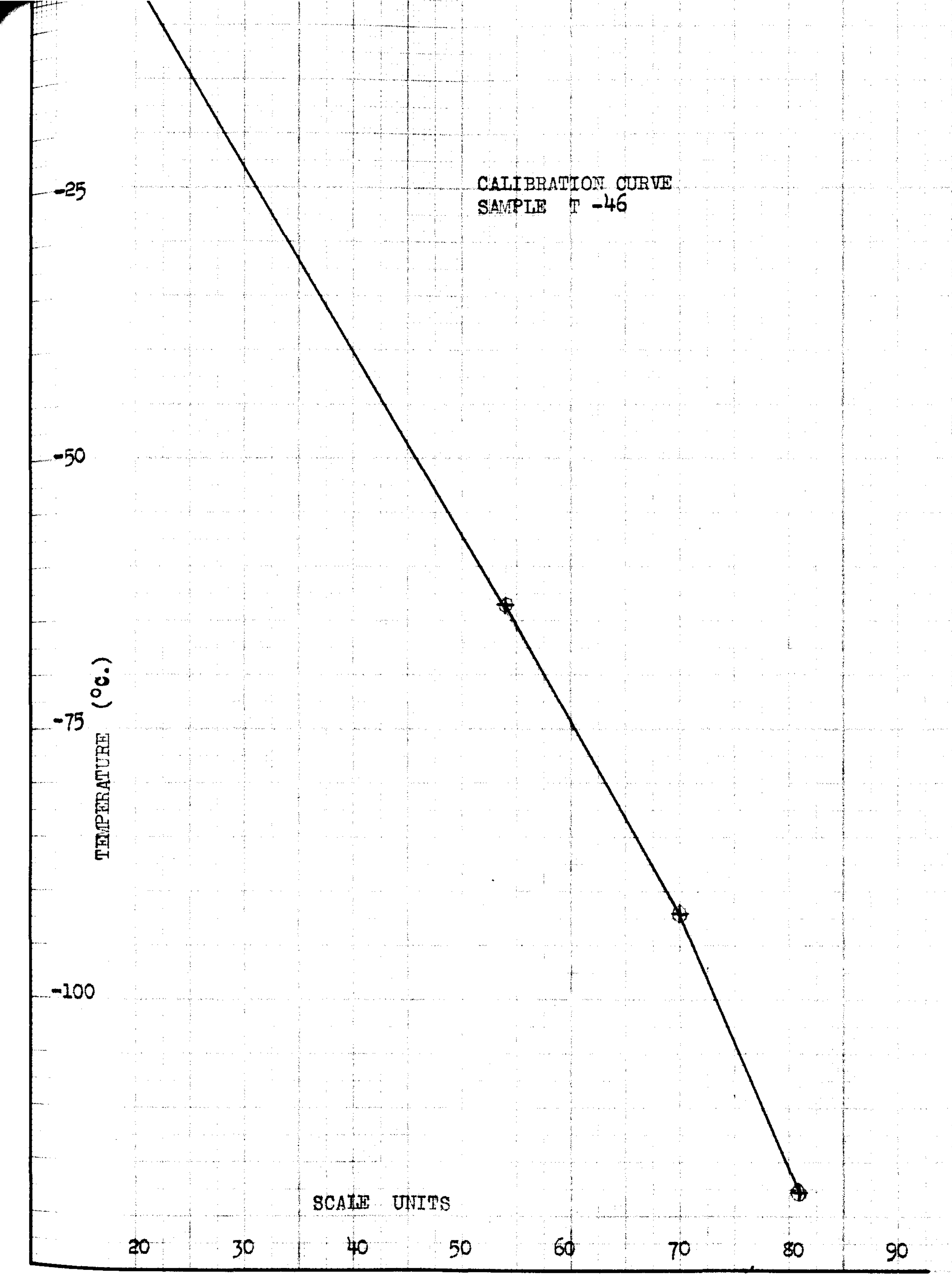


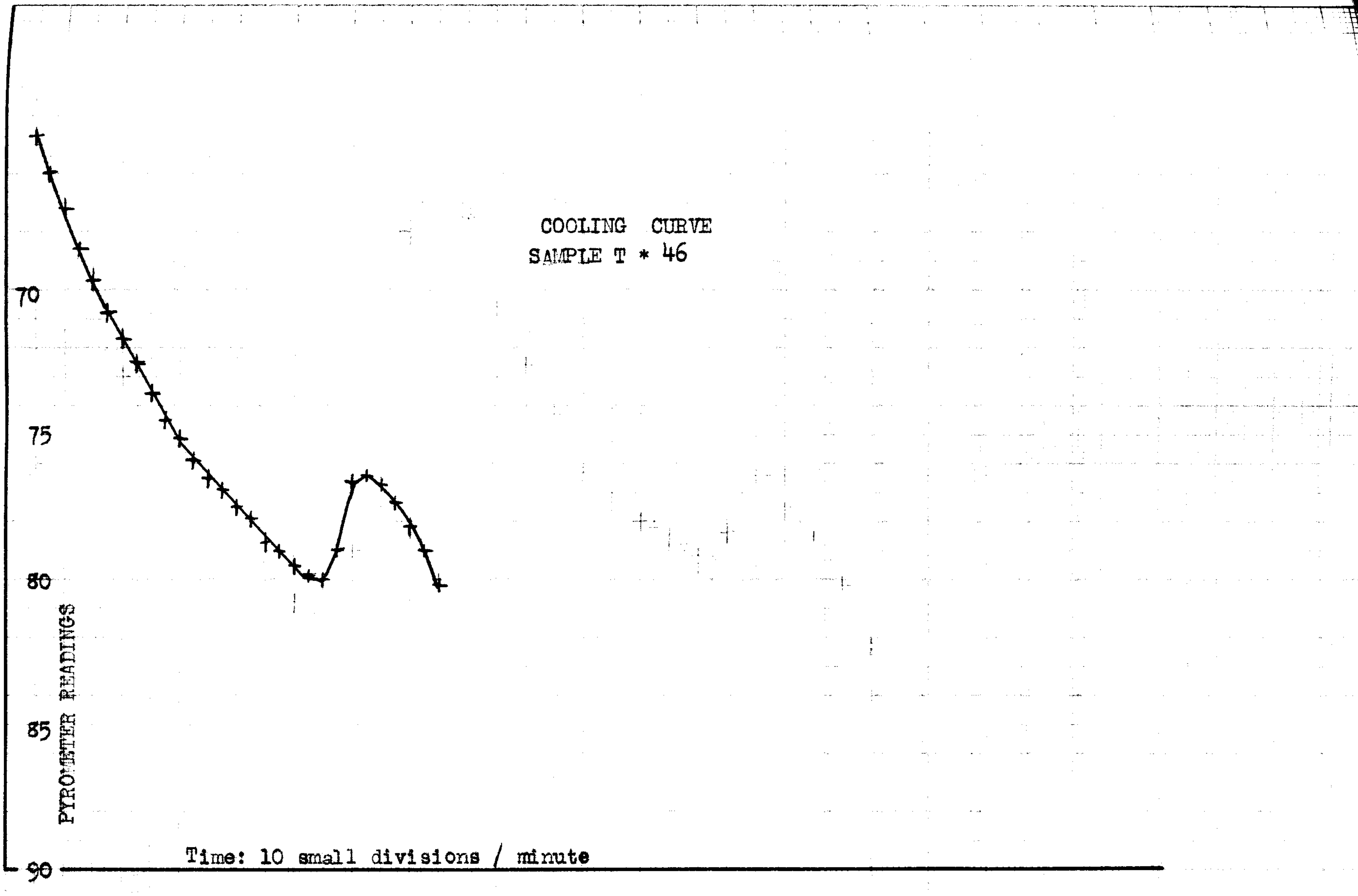
COOLING CURVE
SAMPLE T* 45
40
45
50
55
60
PYROMETER READINGS
Time: 10 small
divisions/minute

TABLE IV - 8
COOLING CURVE, SAMPLE T-46

Calibration:	F. P. (^{o}C)	F. P. (Scale Units)
Water	0.0	16.6
Chloroform	-63.5	54.0
Toluene	-92.0	70.0
Ethyl Bromide	-117.8	80.8

Sample	T-46	
Temperatures (Scale Units) at 15 second intervals	61.5	77.5
	63.2	77.9
	64.7	78.7
	65.9	79.0
	67.2	79.5
	68.6	79.8
	69.7	80.0
	70.8	79.0
	71.7	76.6
	72.5	76.4
	73.6	76.7
	74.5	77.3
	75.1	78.2
	75.9	79.0
	76.5	80.2
	76.9	
Freezing Point (Scale Units)		75.2
Freezing Point (^{o}C)		-104.5
Eutectic Temp. (Scale Units)		76.4
Eutectic Temp. (^{o}C)		-107.1


CALIBRATION CURVE
SAMPLE T -46
TEMPERATURE (°c.)
-25
-50
-75
-100
SCALE UNITS
20
30
40
50
60
70
80
90


COOLING CURVE
SAMPLE T * 46
70
75
80
85
90
PYROMETER READINGS
Time: 10 small divisions / minute

V. OBSERVATIONS ON THE SYSTEM BENZENE-ETHYLBENZENE

The tables and graphs which follow contain the observations made on the benzene-ethylbenzene system. Table V-1 gives the compositions of the mixtures prepared in this system. Tables V-2 and following give the calibration points for the thermocouple pyrometer and the temperature observations on the pyrometer for the corresponding groups of samples. These data are plotted in the group of graphs which follow the tables.

TABLE V- 1

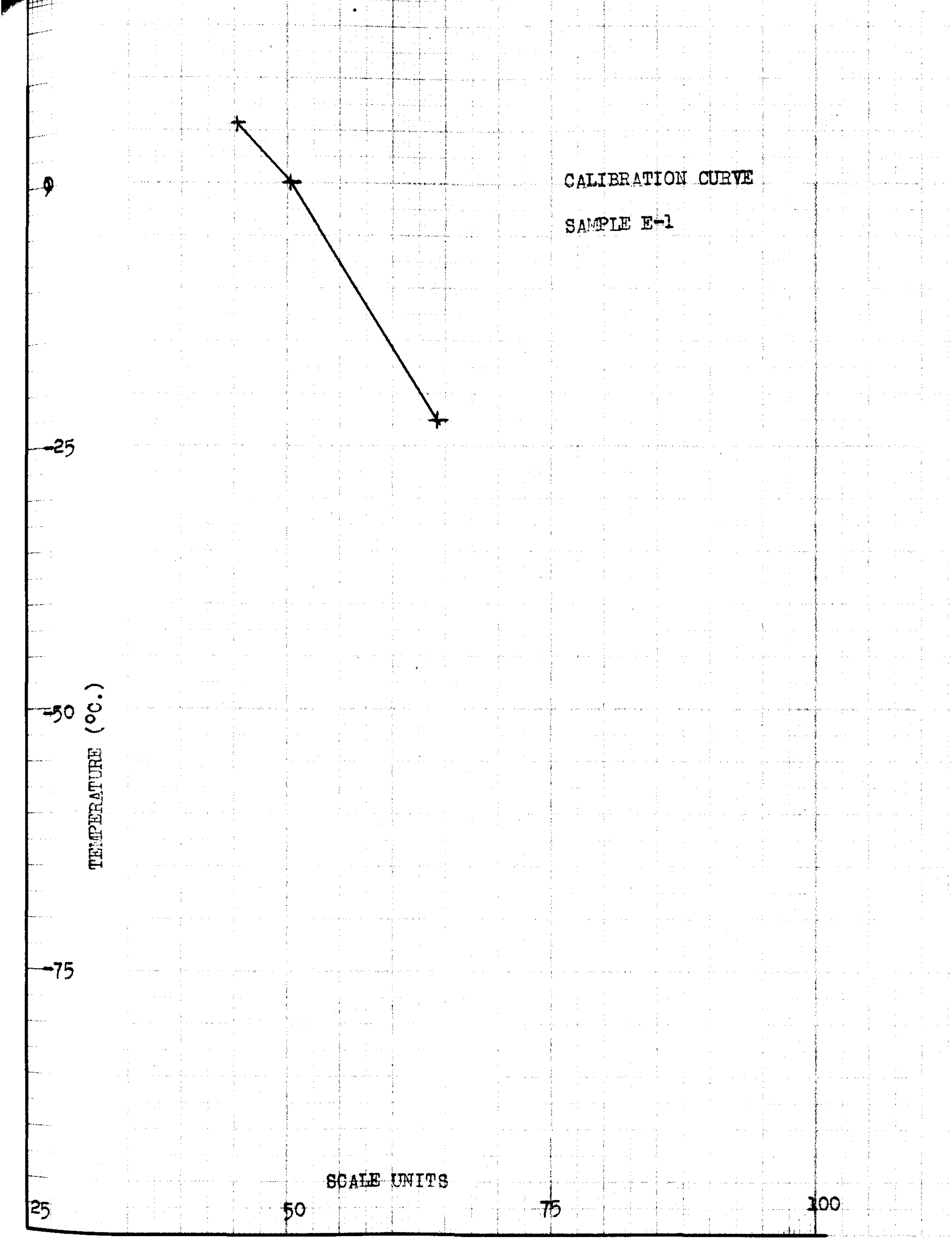
COMPOSITION OF SAMPLES, BENZENE-EHTYLBENZENE SYSTEM

Sample	Weight of Ethylbenzene	Weight of Benzene	Total Weight	Percent Ethylbenzene	Percent Benzene
E-1	0.4886 g	8.5651 g	9.0537 g	5.40	94.60
E-3	1.3231	7.9850	9.3081	14.21	85.78
E-4	1.8032	7.0671	8.8703	20.32	79.67
E-5	2.2265	6.7429	8.9694	24.82	75.17
E-6	2.6236	6.1794	8.8030	29.80	70.20
E-7	3.0985	5.8205	8.9190	34.74	65.26
E-8	3.5021	5.3056	8.8077	39.76	60.24
E-9	3.9816	5.0640	9.0456	44.02	55.98
E-10	4.2708	4.4237	8.6945	49.13	50.88
E-11	4.6695	3.9445	8.6140	54.21	45.79
E-12	5.2883	3.5265	8.8148	59.99	40.01
E-13	5.7334	3.0040	8.7374	65.62	34.39
E-14	6.3094	2.8353	9.1447	69.00	31.01
E-17	7.8795	0.8510	8.7305	90.25	9.75
E-19	8.3393	0.4962	8.8355	94.38	5.62
E-20	7.3248	1.5293	8.8541	82.73	17.27
E-21	7.5578	1.1160	8.6738	87.13	12.87
E-22	7.8041	0.8803	8.6844	89.86	10.14

TABLE V - 2
COOLING CURVE, SAMPLE E-1

Calibration:	F. P. (°C)	F. P. (Scale Units)
Benzene	5.5	45.2
Water	0.0	50.4
Carbon Tetrachloride	-22.6	64.2

Sample	E-1	E-1
Temperatures (Scale Units) at 15 second intervals	38.0 44.6 47.0 47.2 47.4 47.4 47.7	37.2 42.7 47.0 47.2 47.3 51.0
Freezing Point (Scale Units)	46.8	46.9
Freezing Point (°C)	4.0	3.9


CALIBRATION CURVE
SAMPLE E-1
0
-25
-50
-75
TEMPERATURE (°C.)
SCALE UNITS
25
50
75
100

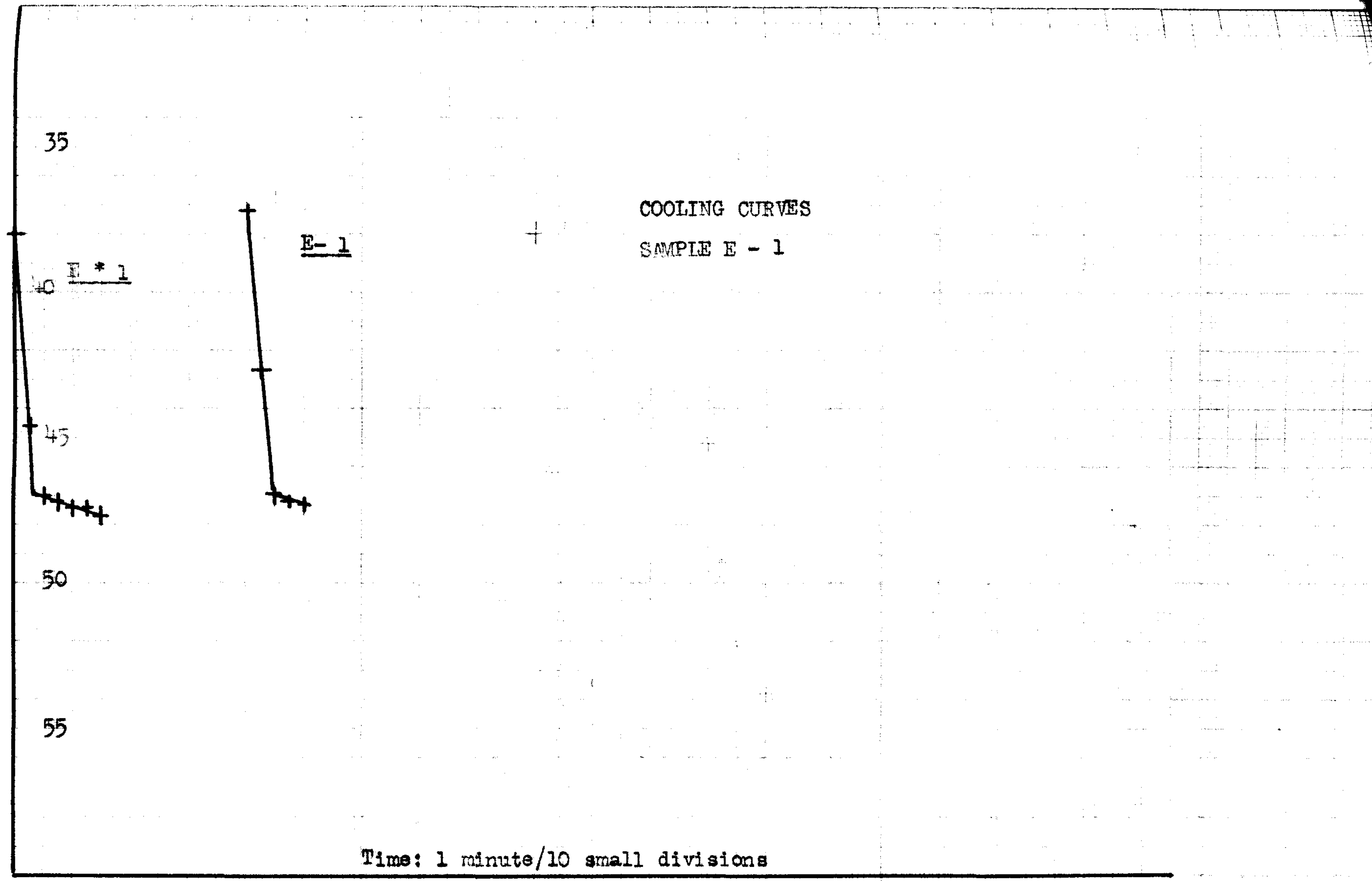
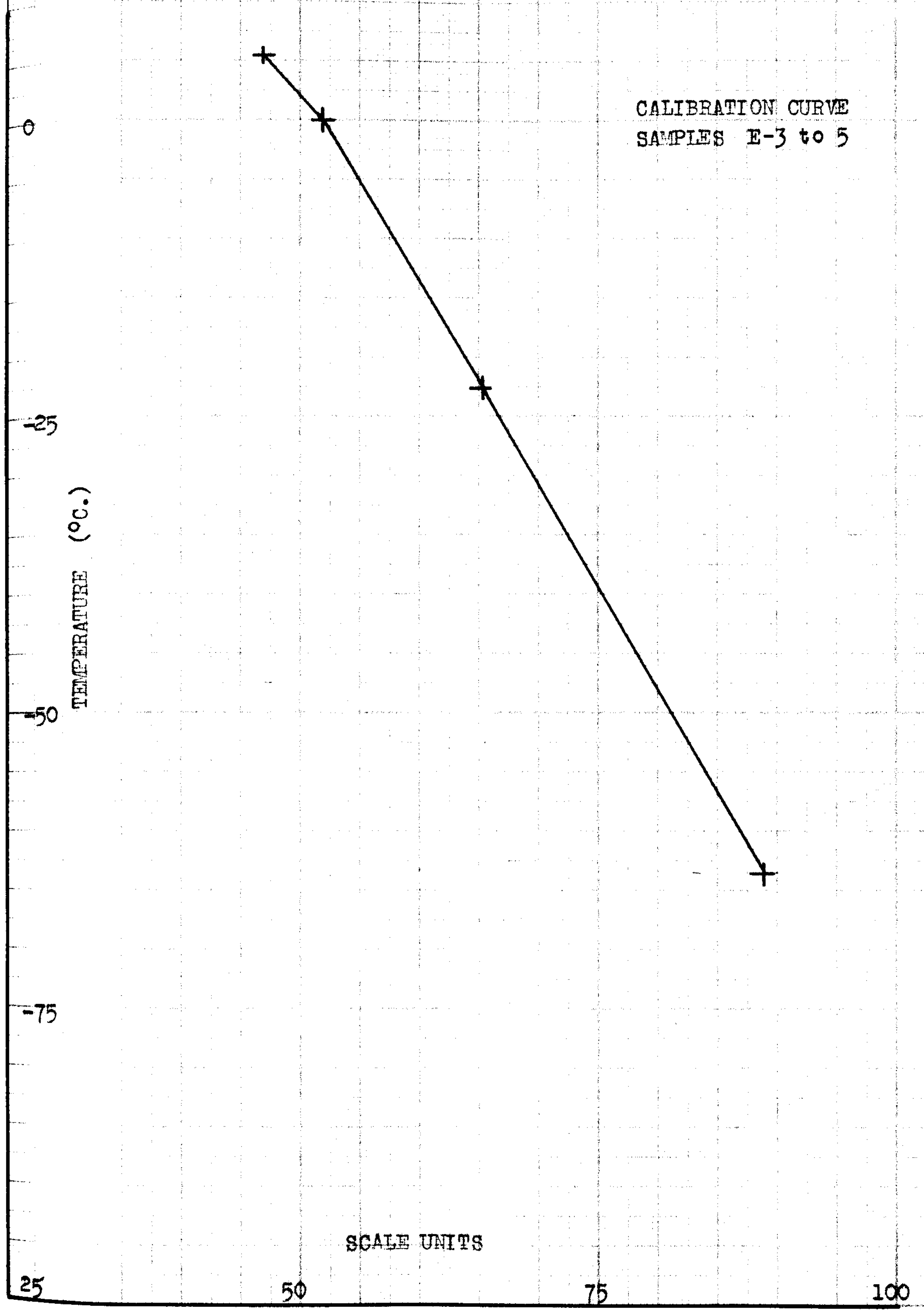

COOLING CURVES
SAMPLE E - 1
E - 1
E * 1
35
40
45
50
55
Time: 1 minute/10 small divisions

TABLE V - 3

COOLING CURVES, SAMPLES E-3 - 5, inclusive

Calibration:	F. P. (°C)	F. P. (Scale Units)
Benzene	5.5	46.8
Water	0.0	51.8
Carbon Tetrachloride	-22.6	65.3
Chloroform	-63.5	88.9

Sample	E-3	E-4	E-5
Temperatures (Scale Units) at 15 second intervals	40.2	36.8	43.3
	45.3	41.2	48.1
	52.2	47.2	54.1
	53.8	53.8	57.2
	54.7	56.2	58.6
	55.8	57.2	59.6
	56.8	58.4	60.2
		59.6	
Freezing Point (Scale Units)	53.1	55.3	56.5
Freezing Point (°C)	-2.0	-5.6	-7.7


CALIBRATION CURVE
SAMPLES E-3 to 5
TEMPERATURE (°C.)
0
-25
-50
-75
SCALE UNITS
25
50
75
100

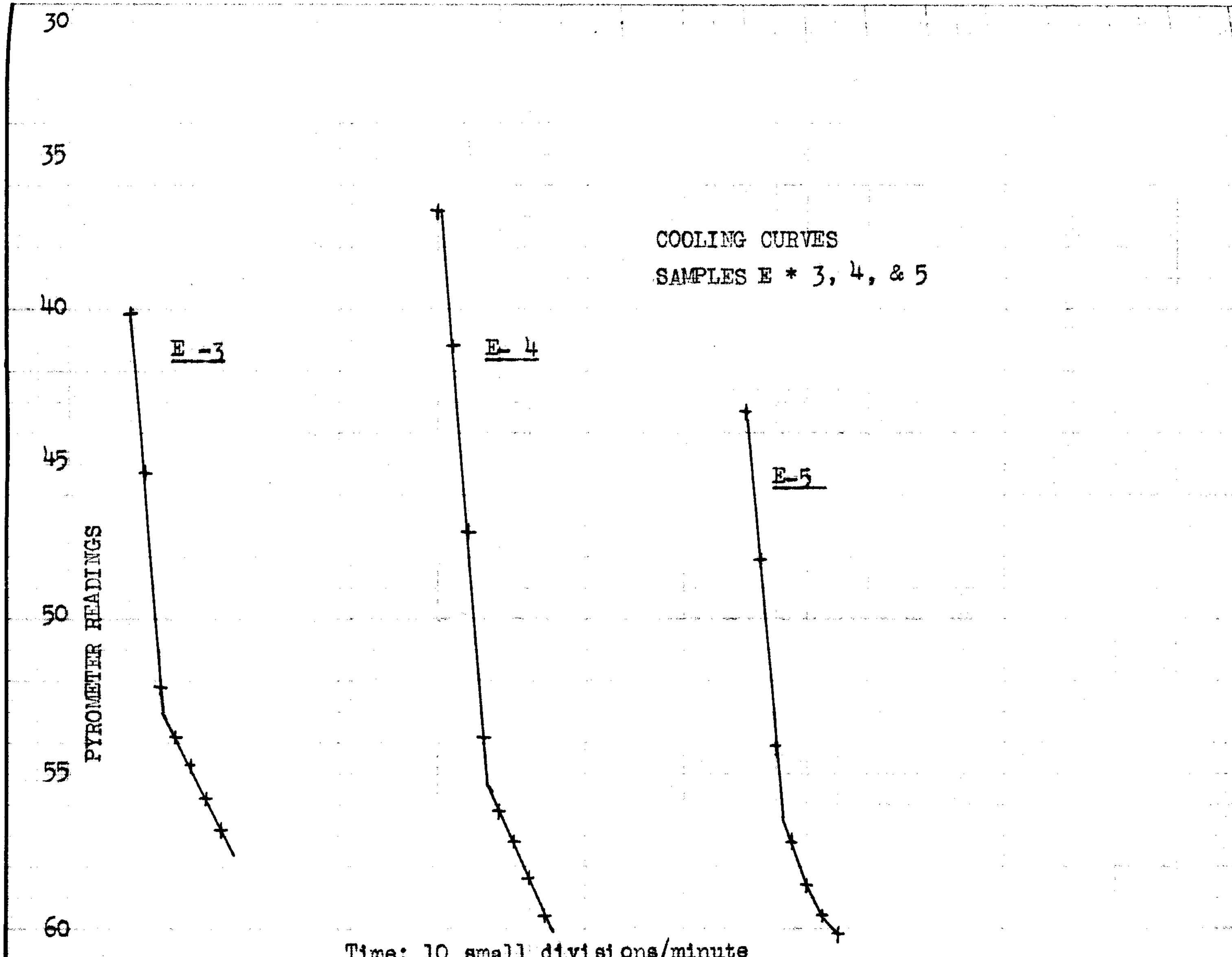
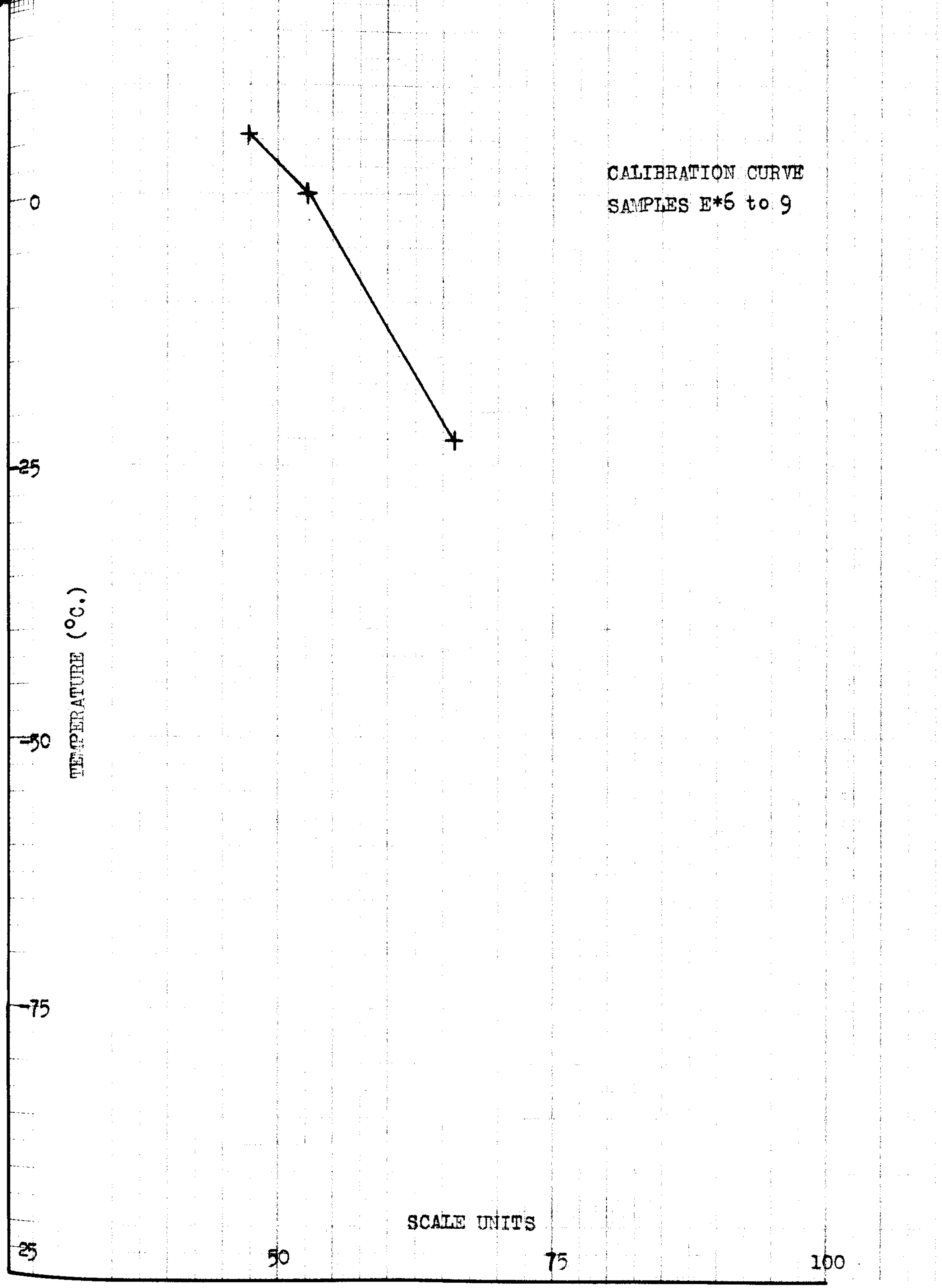

30
35
40
45
50
55
60
PYROMETER READINGS
COOLING CURVES
SAMPLES E * 3, 4, & 5
E -3
E- 4
E-5
Time: 10 small divisions/minute

TABLE V - 4

COOLING CURVES, SAMPLES E-6 - 9, inclusive

Calibration	F. P. (^{o}C)	F. P. (Scale Units)
Benzene	5.5	47.2
Water	0.0	52.6
Carbon Tetrachloride	-22.6	66.0

Sample	E-6	E-7	E-8	E-9
Temperatures (Scale Units) at 15 second intervals	41.8	53.2	45.8	44.8
	45.1	58.6	50.7	48.2
	50.7	62.3	55.3	50.3
	55.8	63.3	59.3	55.0
	59.9	64.7	62.9	58.8
	61.1	66.3	65.2	62.6
	62.2	67.9	66.1	65.2
	63.3	69.2	67.8	67.8
	64.5		69.1	68.9
			70.3	70.1
				71.3
Freezing Point (Scale Units)	60.0	62.2	64.6	67.0
Freezing Point (^{o}C)	-12.3	-16.0	-20.3	-24.2



CALIBRATION CURVE
SAMPLES E*6 to 9
0
-25
-50
-75
25
50
75
100
TEMPERATURE (°C.)
SCALE UNITS

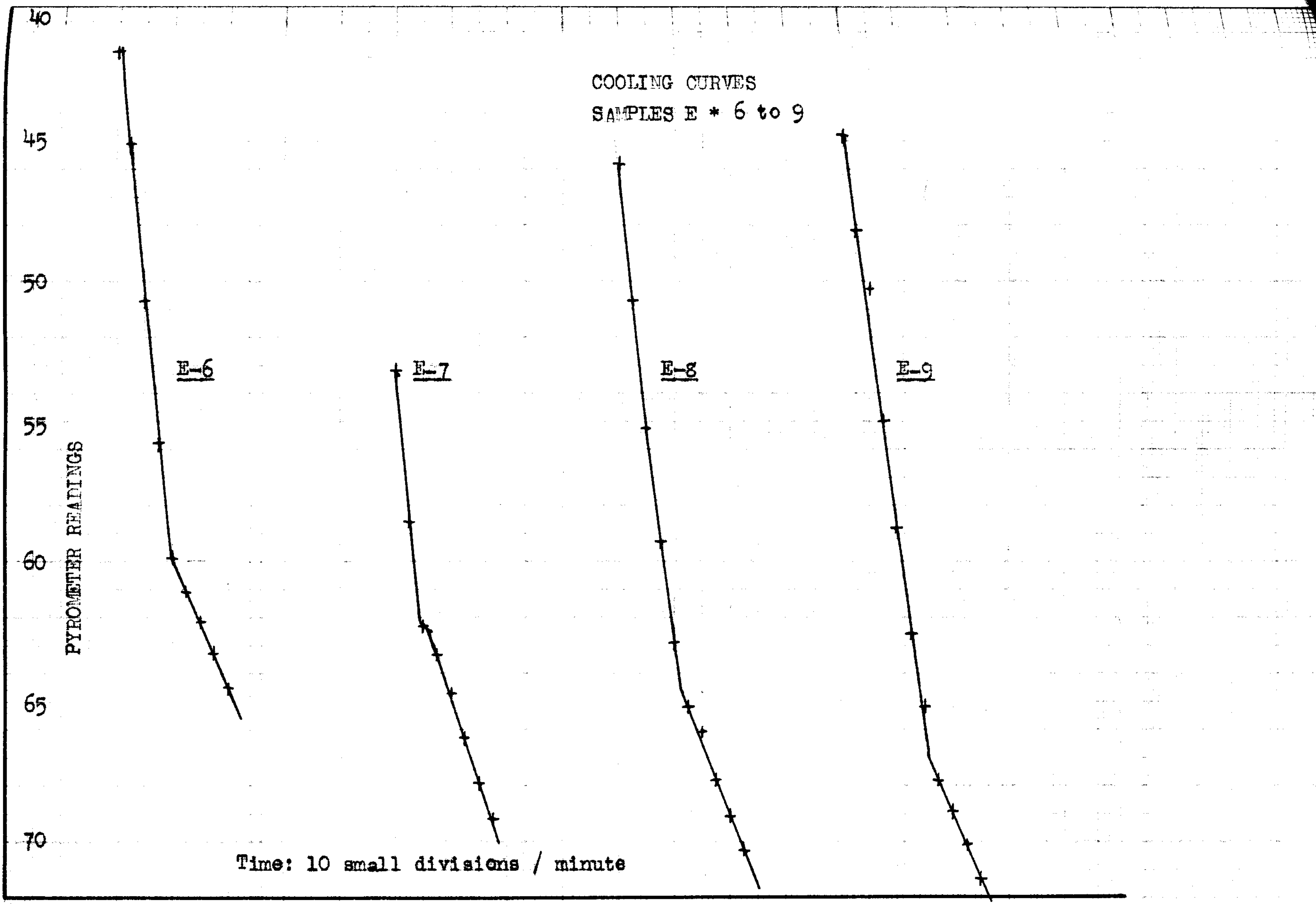
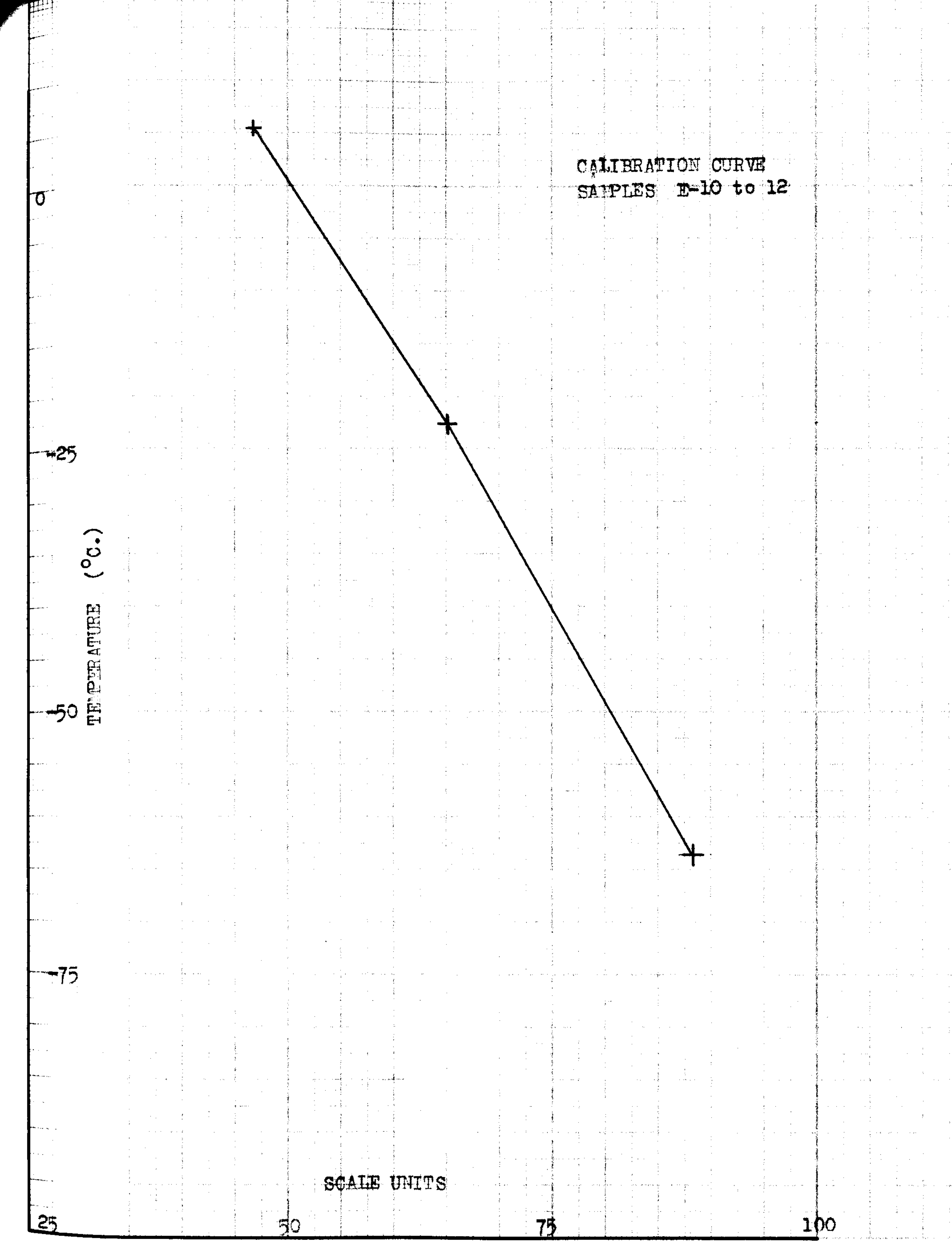

COOLING CURVES
SAMPLES E * 6 to 9
E-6
E-7
E-8
E-9
PYROMETER READINGS
40
45
50
55
60
65
70
Time: 10 small divisions / minute

TABLE V - 5

COOLING CURVES, SAMPLES E-10 - 12, inclusive

Calibration:	F. P. (°C)	F. P. (Scale Units)
Benzene	5.5	46.7
Carbon Tetrachloride	-22.6	65.1
Chloroform	-63.5	88.2

Sample	E-10	E-11	E-12
Temperatures (Scale Units) at 15 second intervals	51.1	53.8	55.1
	54.8	58.0	59.2
	58.3	61.1	62.5
	61.5	63.9	64.8
	64.1	66.2	67.5
	66.6	68.5	70.0
	68.5	70.8	72.2
	69.7	71.4	73.8
	70.5	72.6	74.0
	71.4	73.8	75.6
	72.3	74.9	
Freezing Point (Scale Units)	69.8	70.8	73.4
Freezing Point (°C)	-29.2	-32.7	-37.5


CALIBRATION CURVE
SAMPLES E-10 to 12
TEMPERATURE (°C.)
0
-25
-50
-75
SCALE UNITS
25
50
75
100

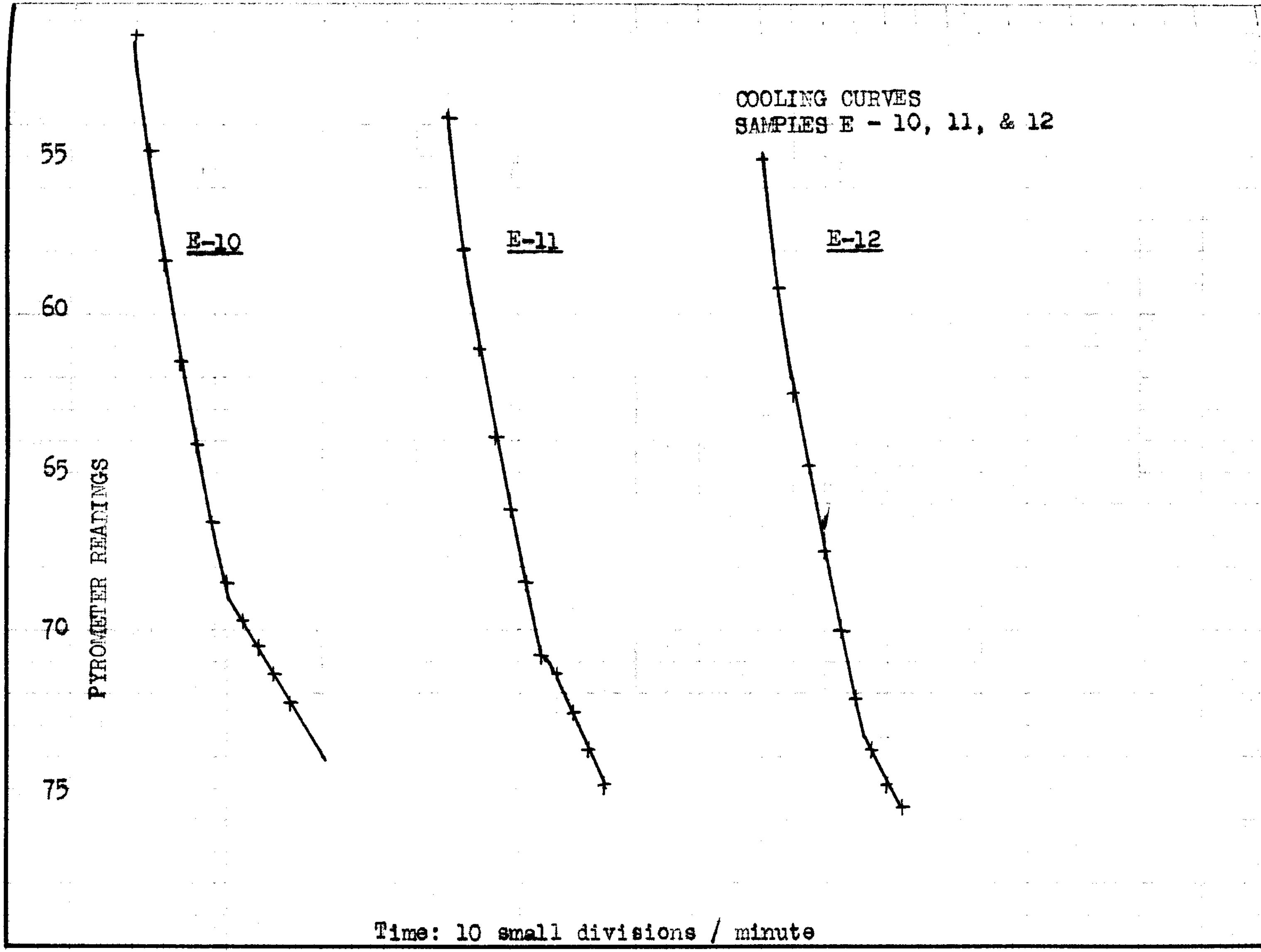
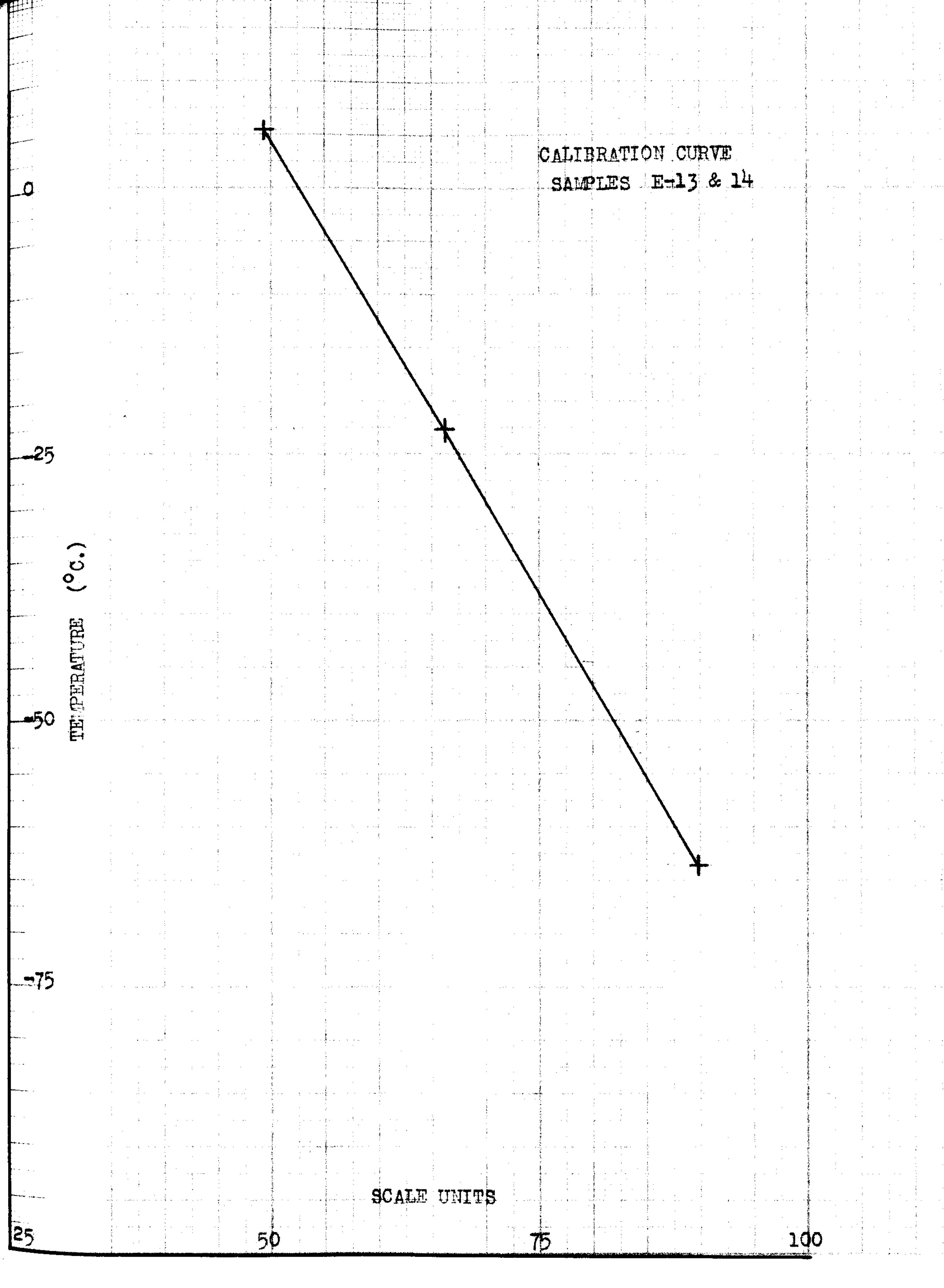

COOLING CURVES
SAMPLES E - 10, 11, & 12
E-10
E-11
E-12
55
60
65
70
75
PYROMETER READINGS
Time: 10 small divisions / minute

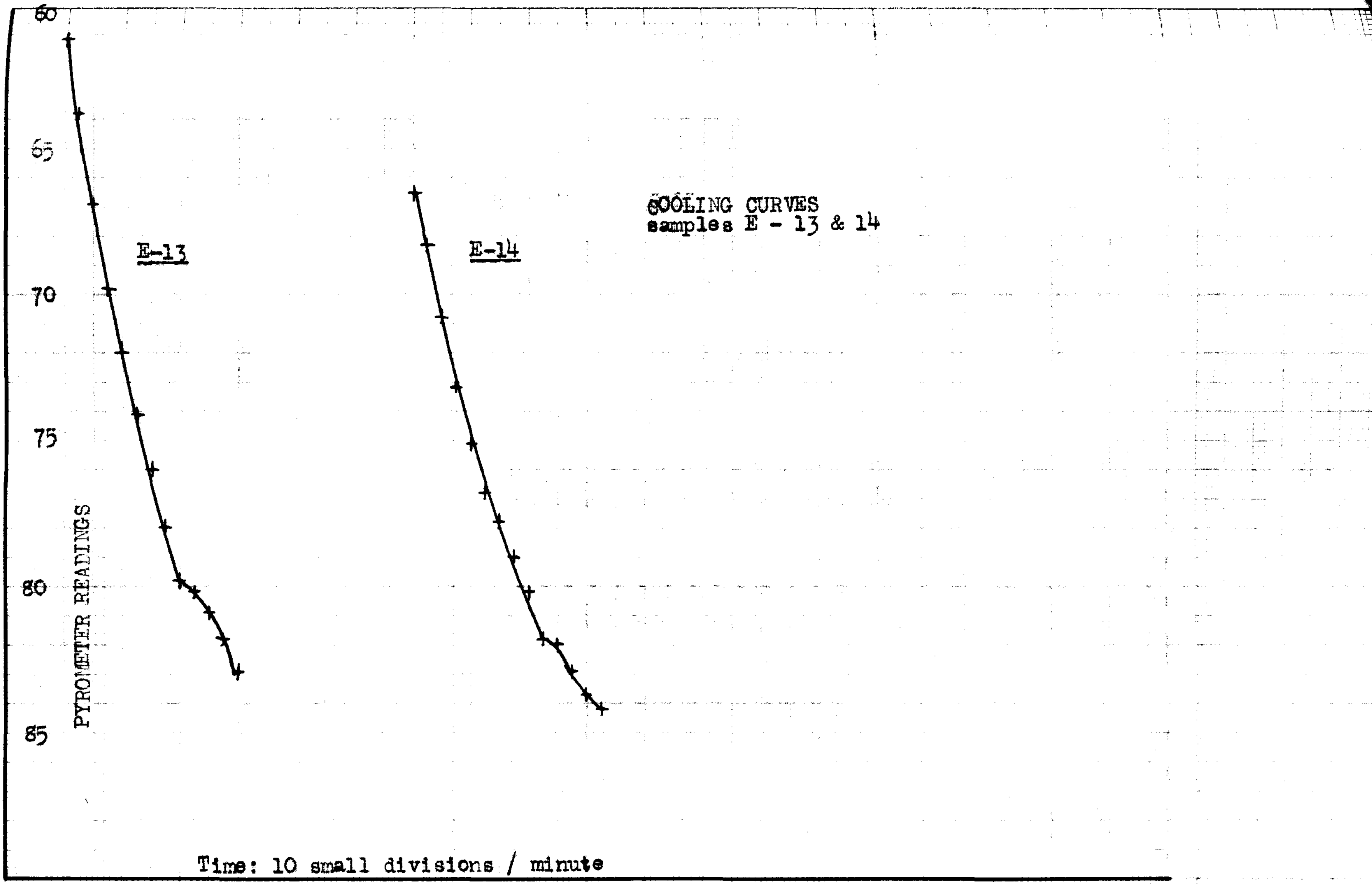
TABLE V - 6

COOLING CURVES, SAMPLES E-13 and 14

Calibration	F. P. (°C)	F. P. (Scale Units)
Benzene	5.5	49.4
Carbon Tetrachloride	-22.6	66.1
Chloroform	-63.5	89.8

Sample	E-13	E-14
Temperatures (Scale Units) at 15 second intervals	61.2	66.5
	63.8	68.3
	66.9	70.8
	69.8	73.2
	72.0	75.1
	74.1	76.8
	76.0	77.8
	78.0	79.0
	79.8	80.2
	80.2	81.8
	80.9	82.0
	81.8	82.9
	82.9	83.7
		84.2
Freezing Point (Scale Units)	79.8	81.8
Freezing Point (°C)	-46.5	-50.0


CALIBRATION CURVE
SAMPLES E-13 & 14
TEMPERATURE (°C.)
0
-25
-50
-75
SCALE UNITS
25
50
75
100



COOLING CURVES
samples E - 13 & 14
E-13
E-14
60
65
70
75
80
85
PYROMETER READINGS
Time: 10 small divisions / minute

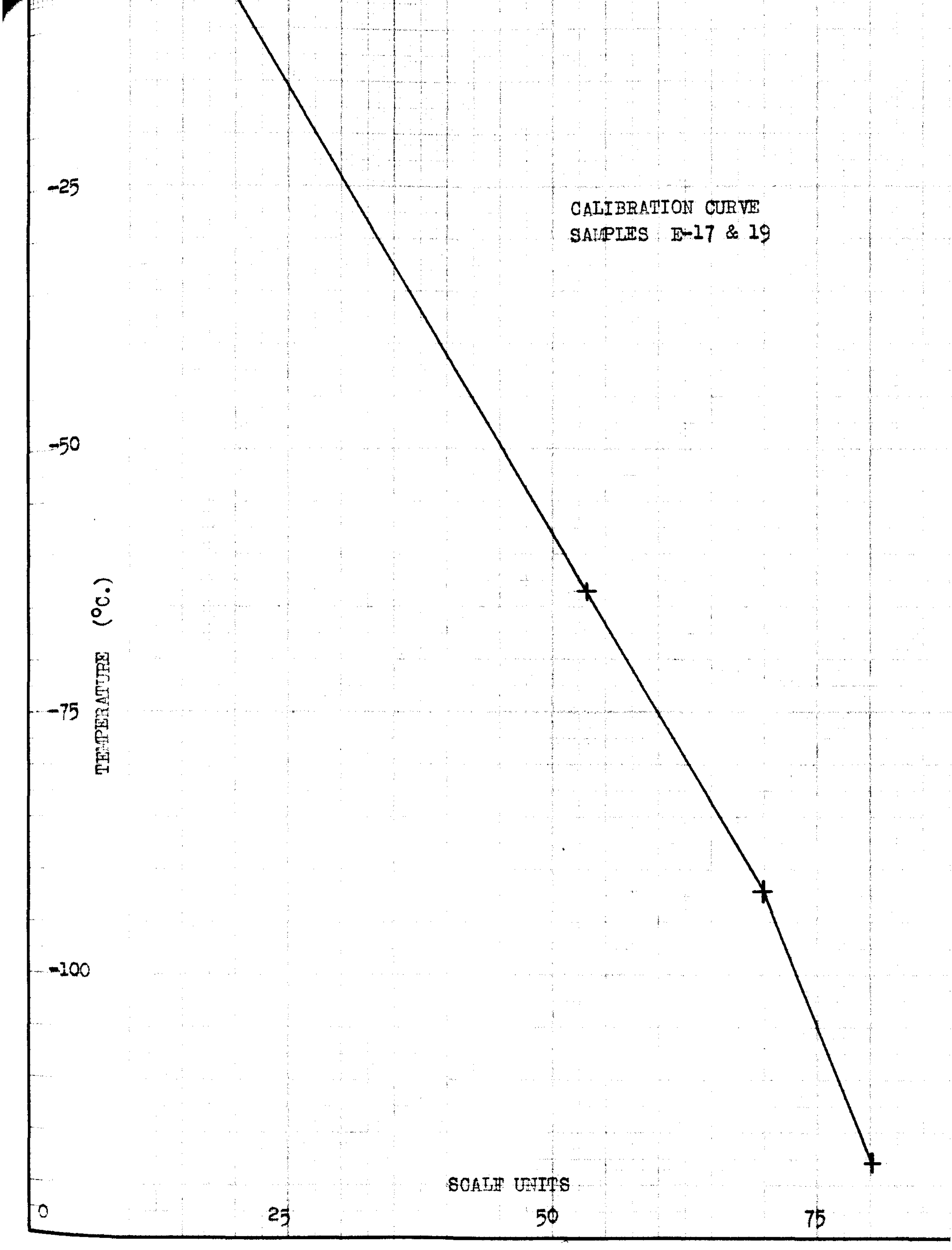
TABLE V - 7

COOLING CURVES, SAMPLES E-17 and 19

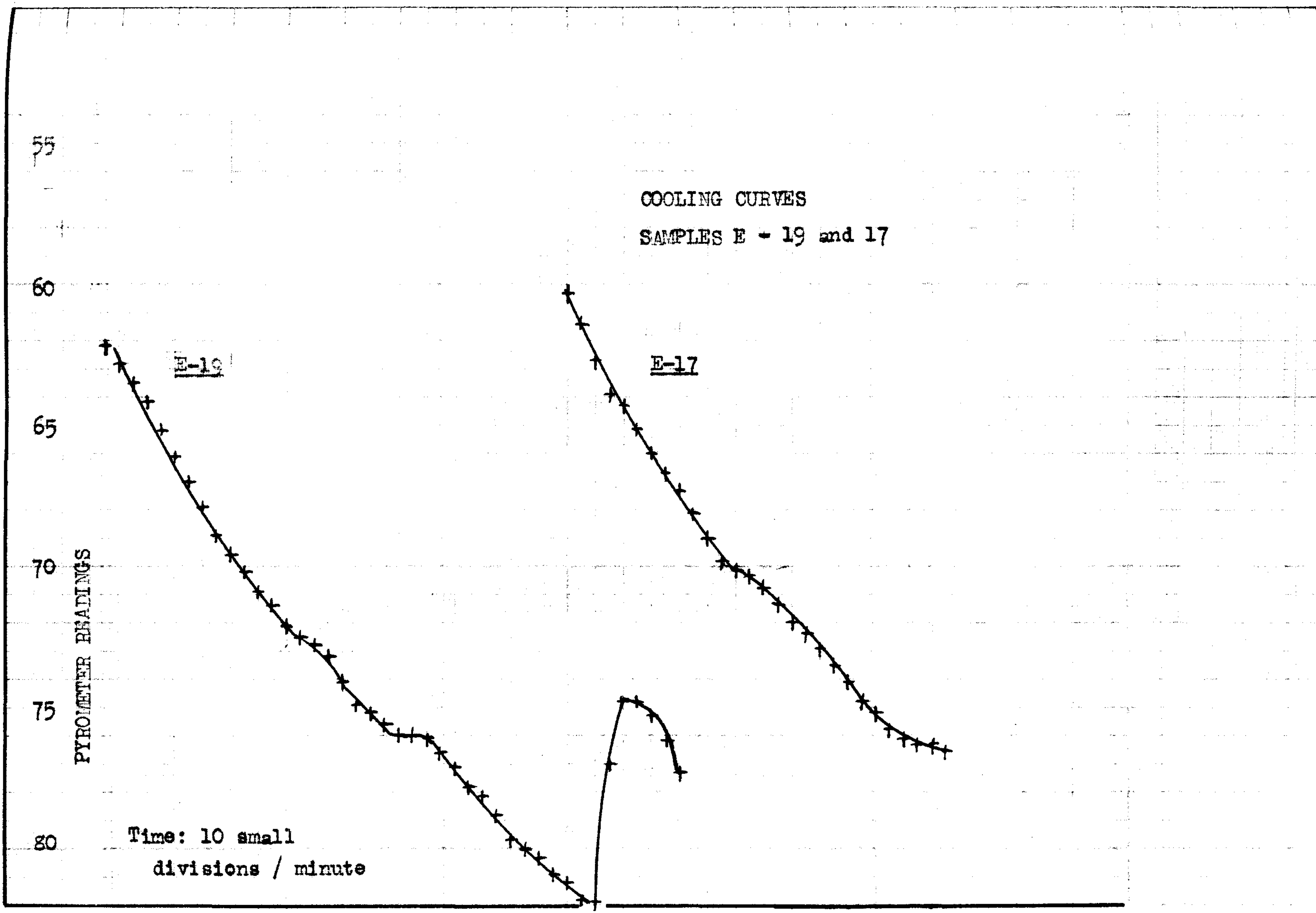
Calibration:		F. P. (^{o}C)	F. P. (Scale Units)
	Water	0.0	15.7
	Chloroform	-63.5	53.1
	Toluene	-92.0	69.9
	Ethyl Bromide	-117.8	80.1

Sample	E-17		E-19		
Temperatures (Scale Units) at 15 second intervals	60.3	71.4	62.2	72.8	79.7
	61.4	72.0	62.8	73.2	80.0
	62.7	72.4	63.5	74.1	80.3
	63.9	72.9	64.2	74.9	80.9
	64.3	73.5	65.2	75.2	81.2
	65.1	74.1	66.1	75.6	81.8
	66.0	74.8	67.0	76.0	81.9
	66.7	75.2	67.9	76.0	77.0
	67.3		68.9	76.6	74.8
	69.0		70.2	77.1	75.3
	69.8		70.9	77.8	76.2
	70.1		71.4	78.1	77.3
	70.3		72.1	78.8	
	70.8		72.5	79.2	

	E-17	E-19
Freezing Point (Scale Units)	-	72.5
Freezing Point (^{o}C)	-	-98.5
Eutectic Temp. (Scale Units)	76.0	74.8
Eutectic Temp. (^{o}C)	-107.3	-104.5



CALIBRATION CURVE
SAMPLES E-17 & 19
TEMPERATURE (°C.)
-25
-50
-75
-100
SCALE UNITS
0
25
50
75



COOLING CURVES
SAMPLES E - 19 and 17
E-19
E-17
55
60
65
70
75
80
PYROMETER READINGS
Time: 10 small divisions / minute

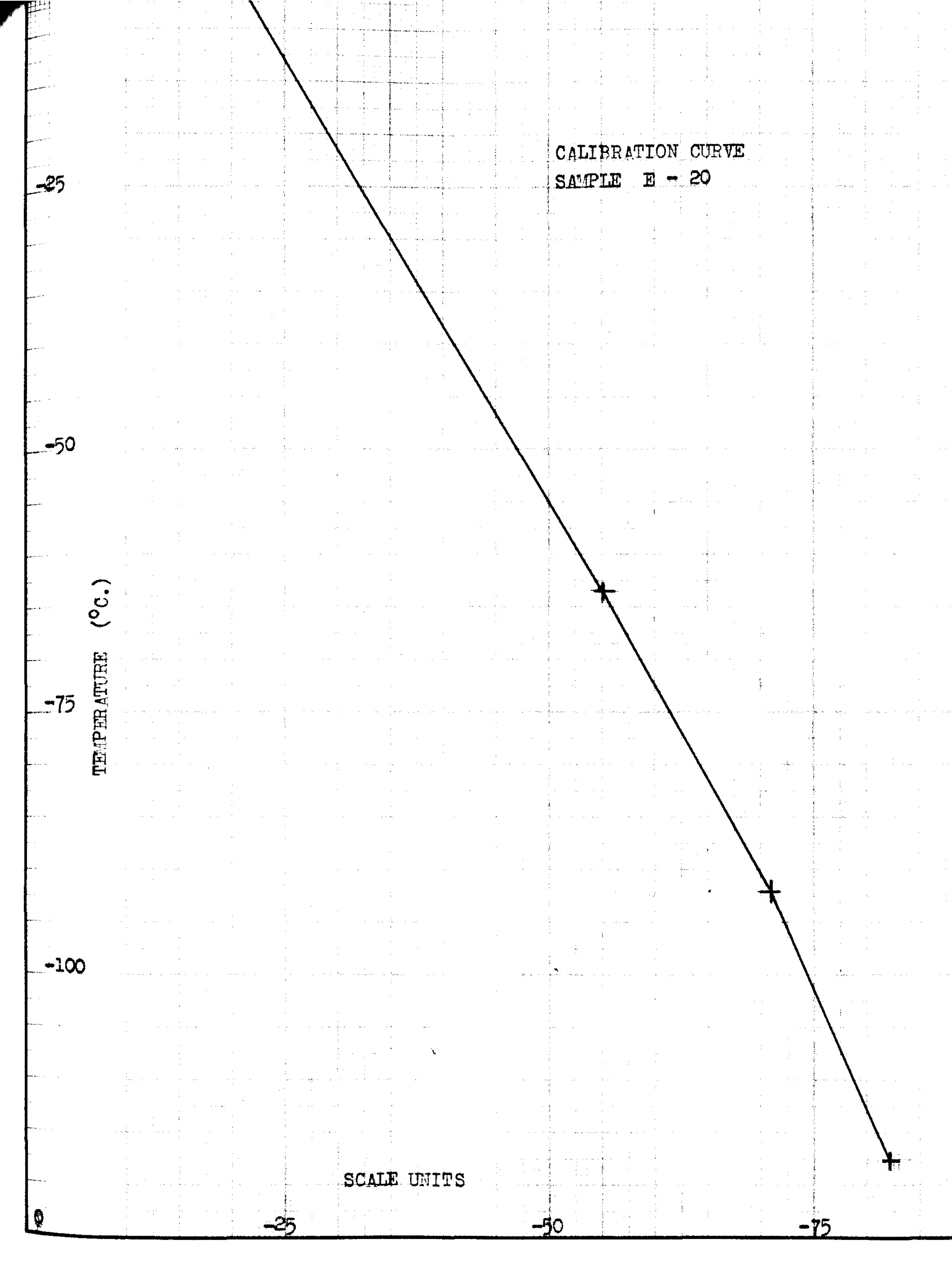
TABLE V - 8

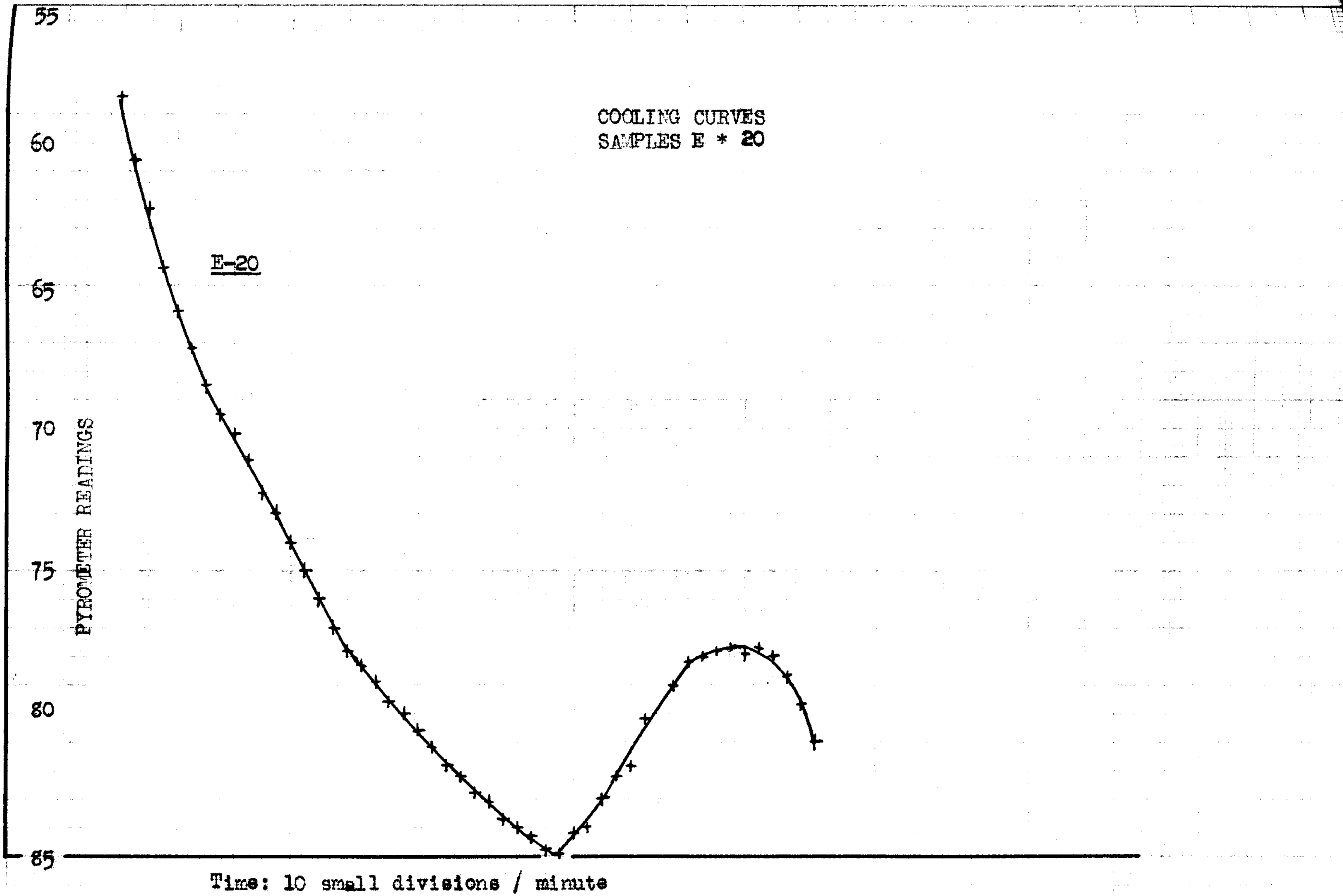
COOLING CURVE, SAMPLE E-20

Calibration:	F. P. (°C)	F. P. (Scale Units)
Water	0.0	17.3
Chloroform	-63.5	55.1
Toluene	-92.0	71.0
Ethyl Bromide	-117.8	83.0

Sample	E-20			
Temperatures (Scale Units) at 15 second intervals	58.4	75.0	83.1	78.2
	60.6	76.0	83.7	78.0
	62.3	77.0	84.0	77.8
	64.1	77.8	84.3	77.7
	65.9	78.3	84.8	77.9
	67.2	78.9	84.9	77.7
	68.5	79.6	84.2	78.0
	69.5	80.0	84.0	78.7
	70.2	80.6	83.0	79.7
	71.1	81.2	82.2	81.0
	72.3	81.8	81.8	
	73.0	82.2	80.2	
	74.0	82.8	79.0	

Freezing Point (Scale Units)	68.8
Freezing Point (°C)	-88.5
Eutectic Temp. (Scale Units)	77.7
Eutectic Temp. (°C)	-107.6


CALIBRATION CURVE
SAMPLE E - 20
TEMPERATURE (°C.)
-25
-50
-75
-100
0
SCALE UNITS
-25
-50
-75



COOLING CURVES
SAMPLES E * 20
E-20
PYROMETER READINGS
55
60
65
70
75
80
85
Time: 10 small divisions / minute

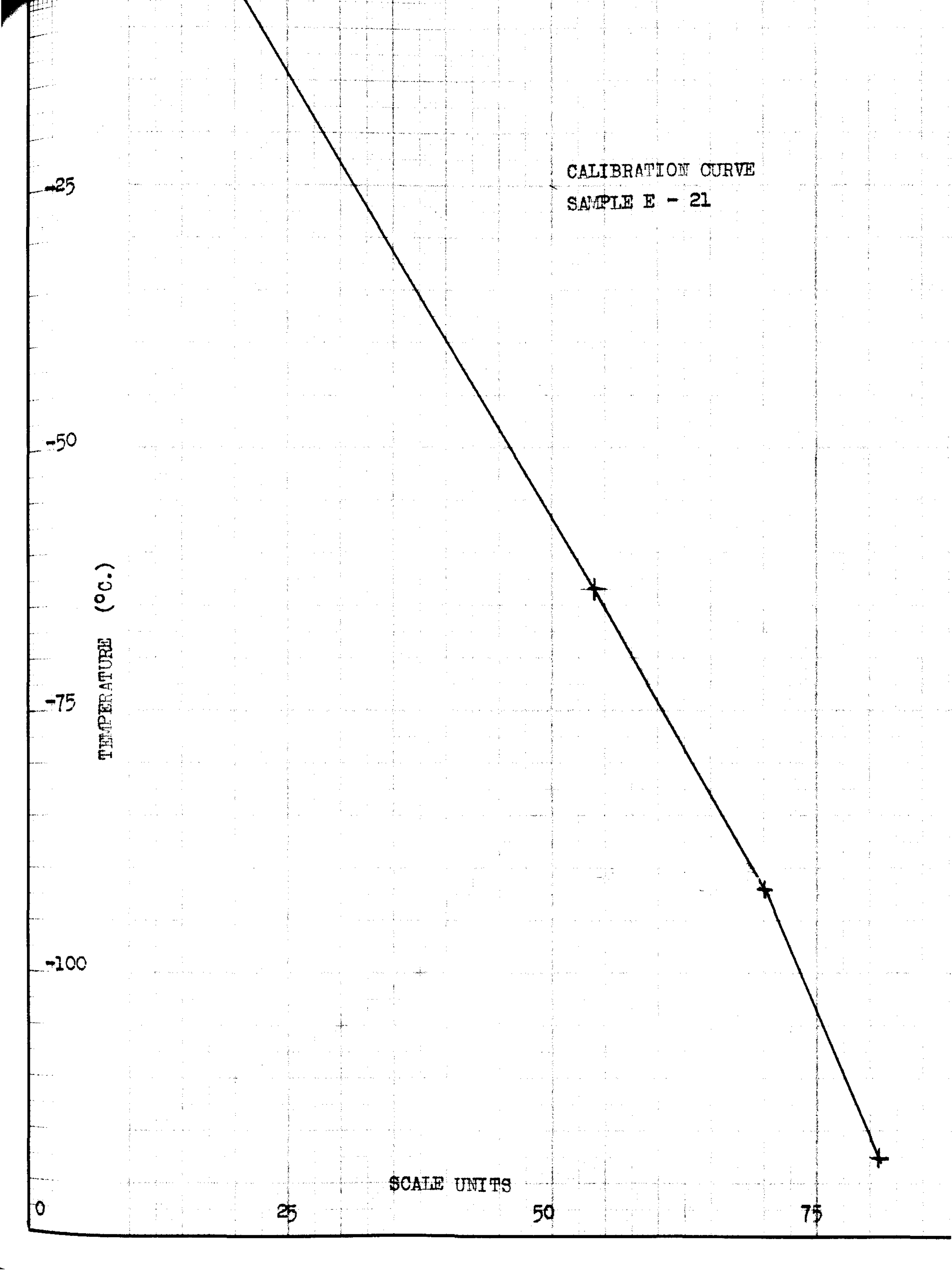
TABLE V - 9

COOLING CURVE, SAMPLE E-21

Calibration:	F. P. (°C)	F. P. (Scale Units)
Water	0.0	16.6
Chloroform	-63.5	54.0
Toluene	-92.0	70.0
Ethyl Bromide	-117.8	80.8

Sample	E-21	
	64.5	73.3
	65.3	75.8
	66.1	76.1
	67.0	76.0
Temperatures	68.0	76.3
(Scale Units)	69.0	77.0
at 15 second	70.2	77.3
intervals	71.0	77.9
	72.0	78.2
	72.9	78.8
	73.3	79.4
	74.2	79.7
	75.0	79.9
	75.7	

Freezing Point (Scale Units)	75.3
Freezing Point (°C)	-104.4
Eutectic Temp. (Scale Units)	76.0
Eutectic Temp. (°C)	-106.0


CALIBRATION CURVE
SAMPLE E - 21
-25
-50
-75
-100
TEMPERATURE (°C.)
0
25
50
75
SCALE UNITS

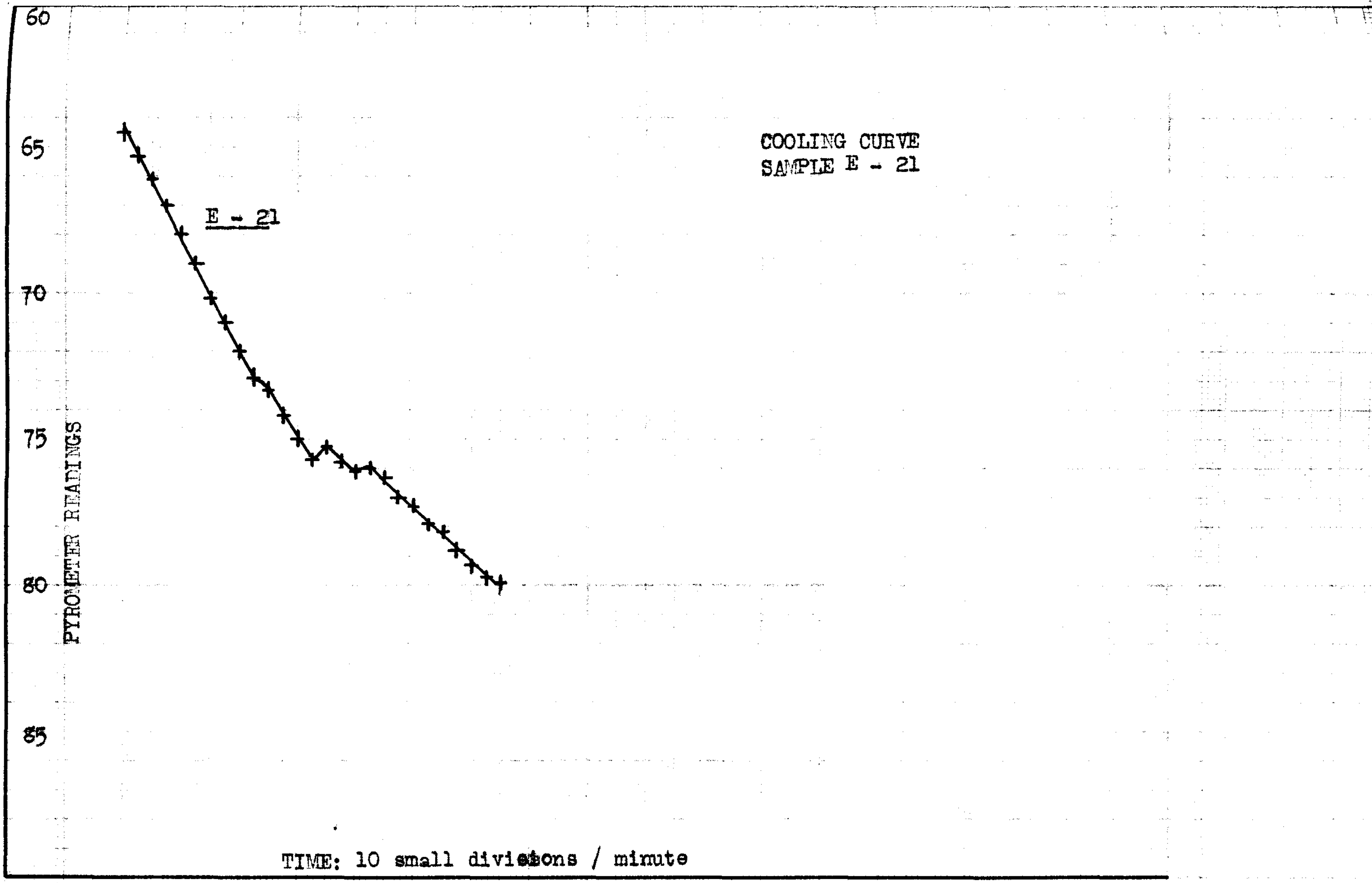

COOLING CURVE
SAMPLE E - 21
E - 21
PYROMETER READINGS
60
65
70
75
80
85
TIME: 10 small divisions / minute

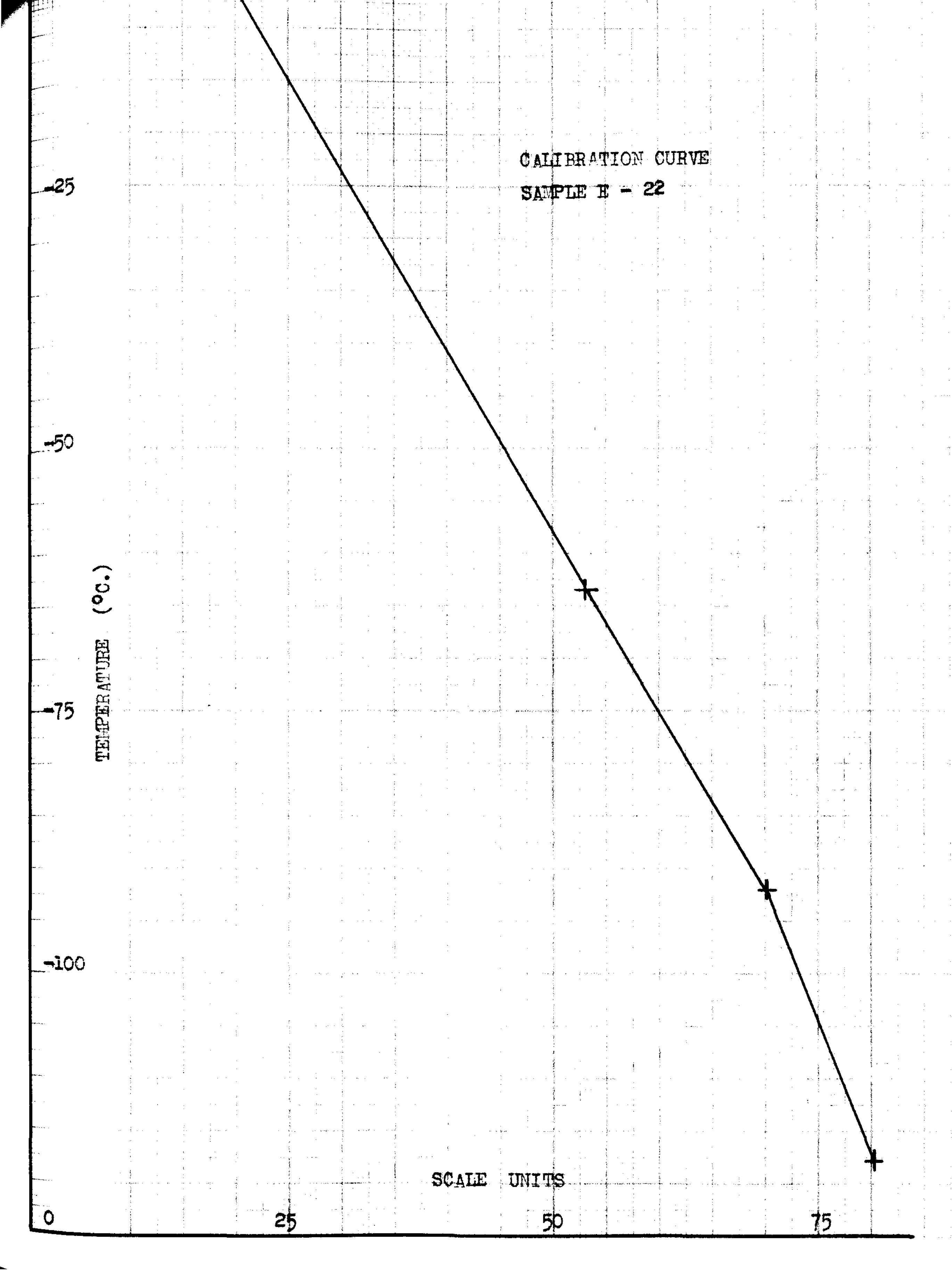
TABLE V - 10

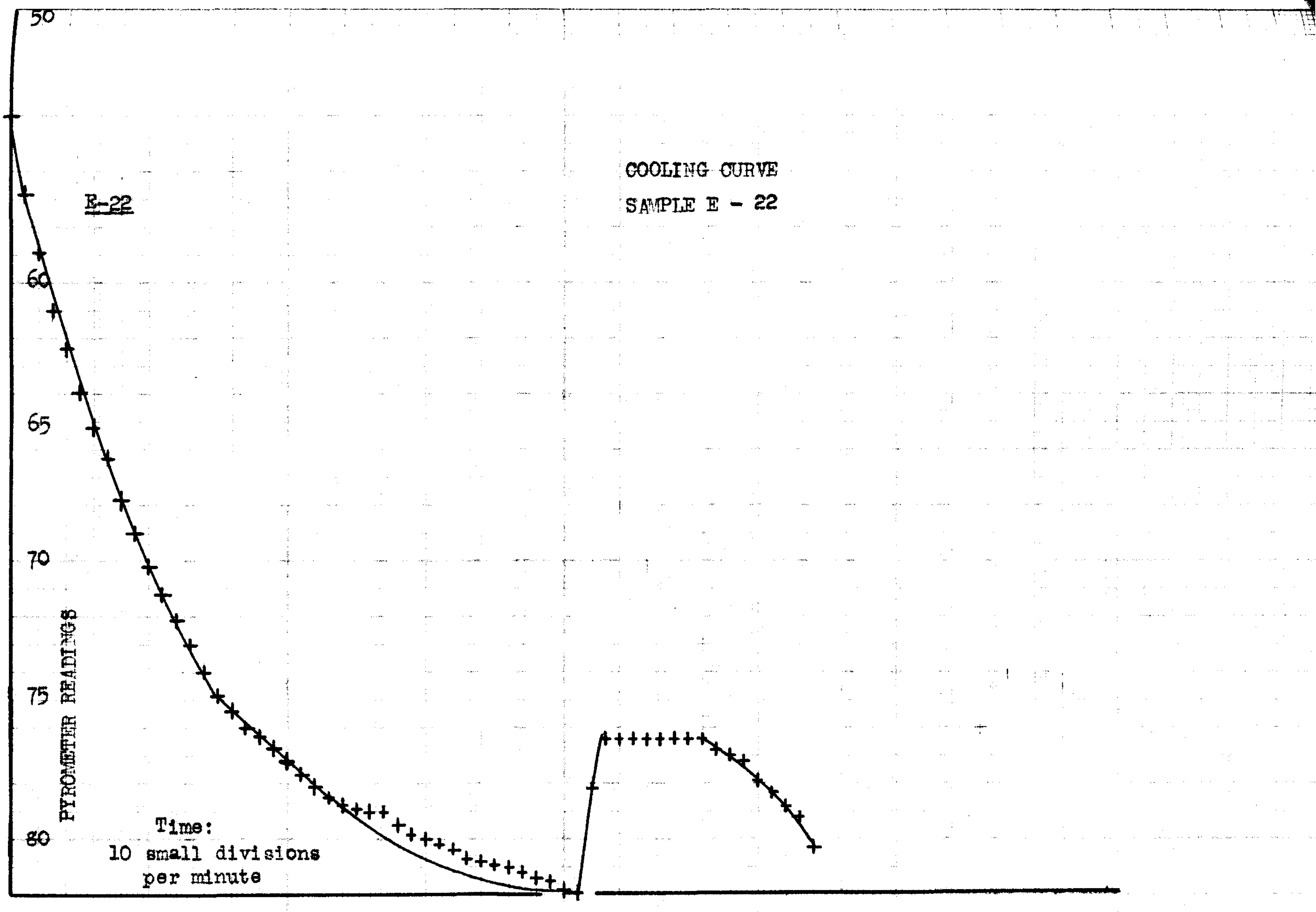
COOLING CURVE, SAMPLE E-22

Calibration:	F. P. (^{o}C)	F. P. (Scale Units)
Water	0.0	16.2
Chloroform	-63.5	53.0
Toluene	-92.0	70.1
Ethyl Bromide	-117.8	80.2

Sample	E-22			
Temperatures (Scale Units) at 15 second intervals	54.0	74.8	80.0	76.4
	56.8	75.4	80.2	76.4
	58.9	76.0	80.4	76.4
	61.0	76.3	80.7	76.4
	62.4	76.7	80.8	76.4
	63.9	77.2	80.7	76.4
	65.2	77.7	81.0	76.8
	66.3	78.1	81.2	77.0
	67.8	78.5	81.4	77.2
	69.0	78.8	81.5	77.9
	70.2	78.9	81.8	78.3
	71.2	79.0	81.7	78.8
	72.1	79.0	78.2	79.2
	73.0	79.5	76.4	80.3
	74.0	79.8	76.4	

Freezing Point (Scale Units)	74.8
Freezing Point (^{o}C)	-103.5
Eutectic Temp. (Scale Units)	76.4
Eutectic Temp. (^{o}C)	-107.8


CALIBRATION CURVE
SAMPLE E - 22
TEMPERATURE (°C.)
SCALE UNITS
-25
-50
-75
-100
0
25
50
75



COOLING CURVE
SAMPLE E - 22
E-22
50
60
65
70
75
80
PYROMETER READINGS
Time:
10 small divisions
per minute

VI. EQUILIBRIUM DIAGRAMS OF THE SYSTEMS

The observed data from the cooling curves of the benzene-toluene system are summarized in Table VI-1. From these data, the equilibrium diagram of the system is plotted. The eutectic point of the system is found at approximately 88.5% toluene, and the mean observed eutectic temperature is -107.3°C. No evidence of appreciable solid solubility was found.

In Table VI-2, the data from the cooling curves of the benzene-ethylbenzene system are summarized. The equilibrium diagram for this system is constructed from these data, and is presented following the table. The mean observed eutectic temperature is -107.2°C., and the eutectic composition is approximately 88.0% ethylbenzene. As in the case of the benzene-toluene system, no evidence of appreciable solid solubility was found.

Both systems are, therefore, simple eutectic systems. The two equilibrium diagrams are plotted together on the graph following the equilibrium diagrams for the individual systems. The following comparisons between the two systems can be seen from this diagram:

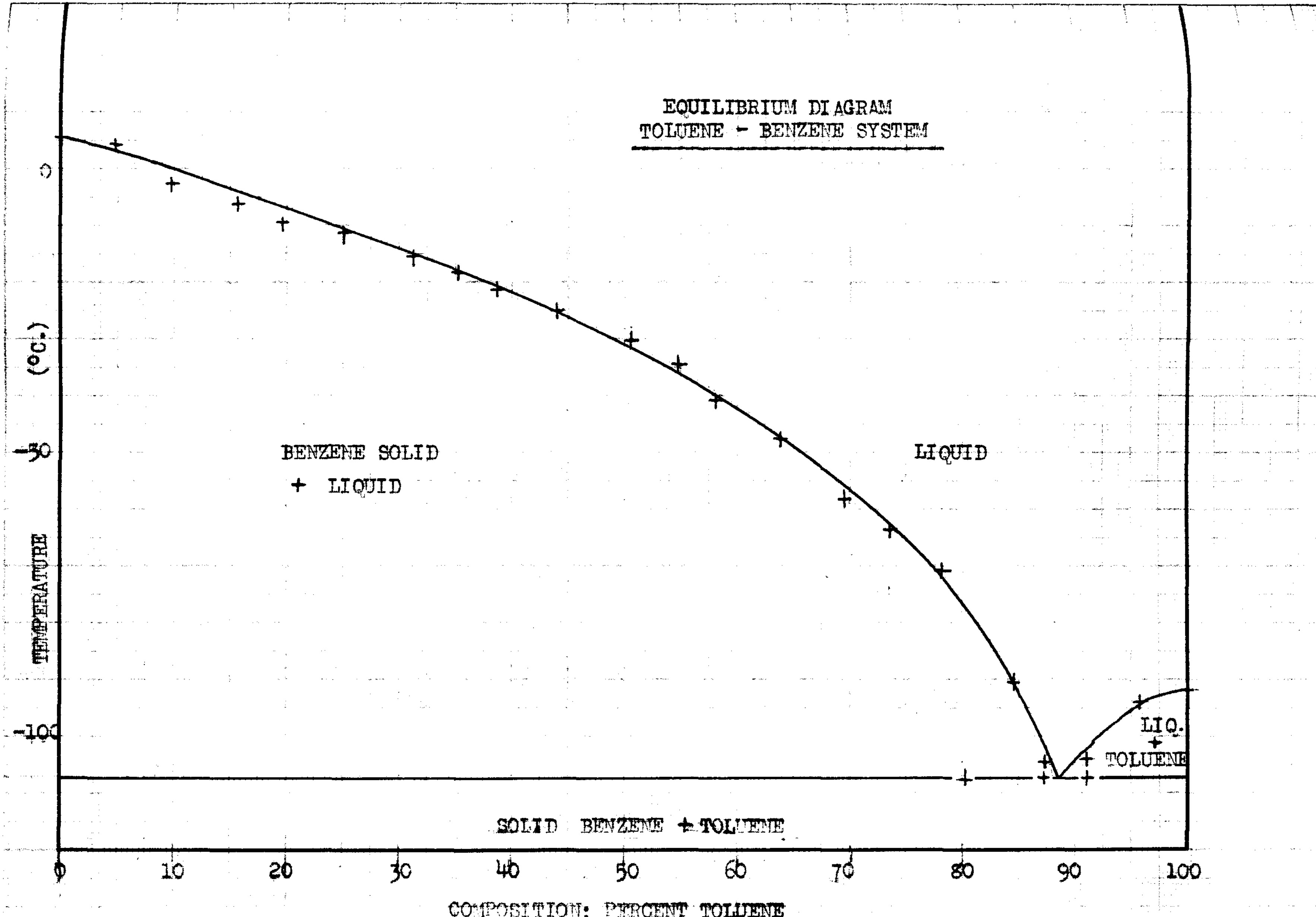
1. The eutectic points of the two systems fall at very nearly the same temperature and compositions.
2. Addition of toluene to benzene causes initially a greater lowering of freezing point for a given weight of addend than does addition of an equal weight of ethylbenzene.

As the latter fact was to have been expected because of the lower molecular weight of toluene as compared to ethylbenzene, it is of interest to construct the equilibrium diagrams of the systems on a mol percent basis, in order to ascertain what effects equimolal additions of toluene and ethylbenzene have on the freezing point. The compositions of the mixtures used in this work are given in mol percent in Tables VI-1 and VI-2; and the equilibrium diagrams of the two systems, with compositions expressed as mol percent, are shown together in the diagram which follows. It will be seen that the differences between the two equilibrium diagrams have practically disappeared. The two diagrams are practically identical until less than 50 mol percent benzene; in this region the benzene-ethylbenzene freezing line is lower than that of the toluene-benzene system, and the benzene-toluene eutectic comes at a lower molal concentration of benzene than does the benzene-ethylbenzene eutectic.

TABLE VI - 1

COMPOSITIONS AND EQUILIBRIUM POINTS OF MIXTURES, BENZENE-TOLUENE SYSTEM

Sample	Percent Toluene by Weight	Mol Percent Toluene	Freezing Point (°C)	Eutectic Temp. (°C)
Benzene	-	-	5.5	-
T-22	4.82	4.08	4.2	
T-23	9176	8.32	-2.5	
T-25	15.57	13.5-	-6.1	
T-26	19.76	17.2	-9.5	
T-27	25.07	22.1	-11.2	
T-28	31.43	28.1	-15.3	
T-29	35.24	31.6	-18.1	
T-30	38.61	35.0	-21.3	
T-31	43.96	39.8	-25.0	
T-32	50.58	46.6	-30.1	
T-33	54.75	50.6	-34.5	
T-34	58.07	53.9	-41.0	
T-35	63.89	59.9	-47.6	
T-36	69.62	65.8	-58.1	
T-37	73.52	70.0	-63.4	
T-38	78.09	75.2	-70.8	
T-45	80.31	78.6	-	-107.7
T-41	84.62	82.4	-90.5	
T-46	87.29	85.3	-104.5	-107.1
T-42	91.11	89.8	-104.0	-107.2
T-43	95.67	95.0	-94.0	
Toluene	100.00	100.00	-92.0	

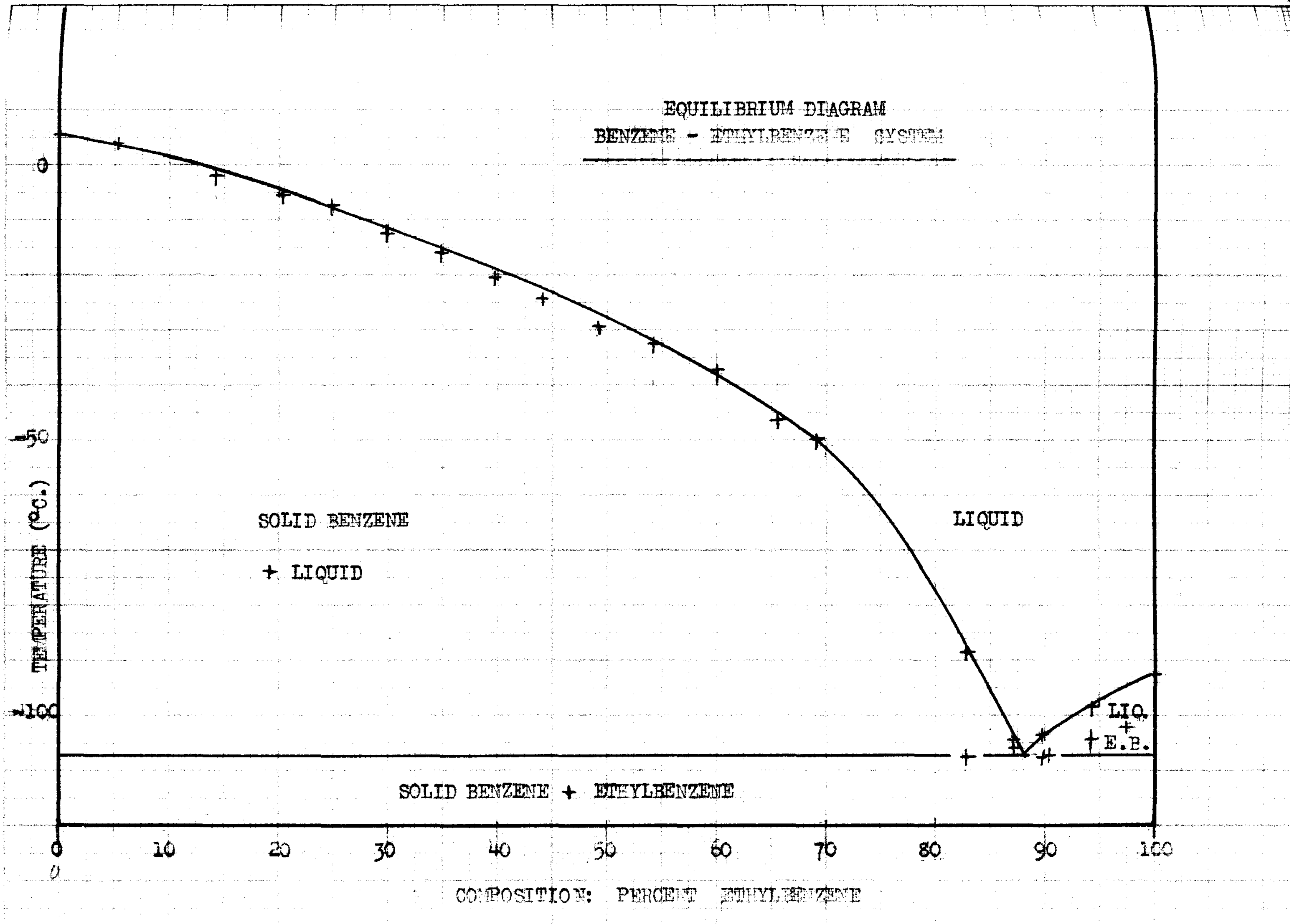


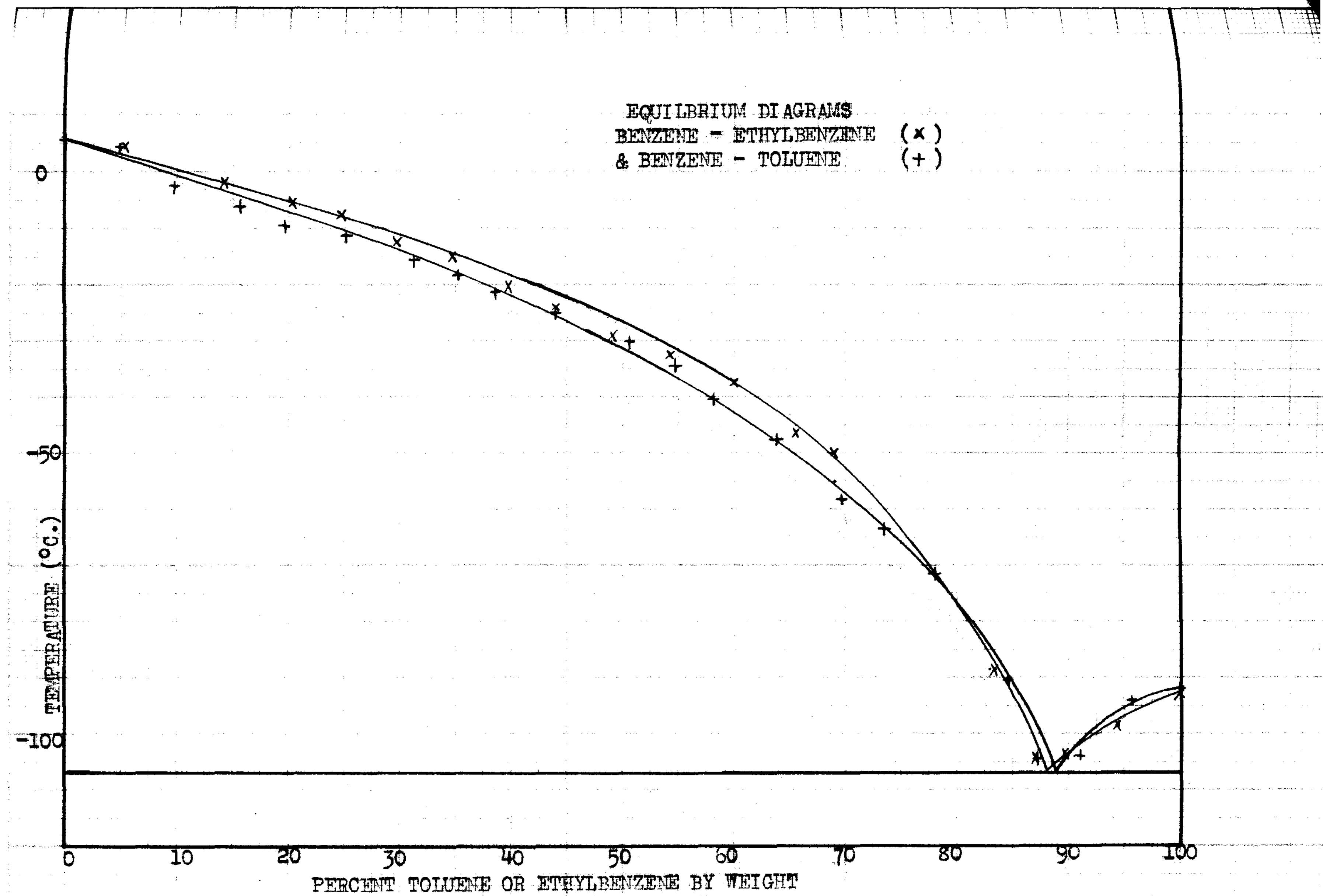
EQUILIBRIUM DIAGRAM
TOLUENE - BENZENE SYSTEM
0
-50
-100
TEMPERATURE (°C.)
BENZENE SOLID
+ LIQUID
LIQUID
LIQ.
+
TOLUENE
SOLID BENZENE + TOLUENE
0
10
20
30
40
50
60
70
80
90
100
COMPOSITION: PERCENT TOLUENE

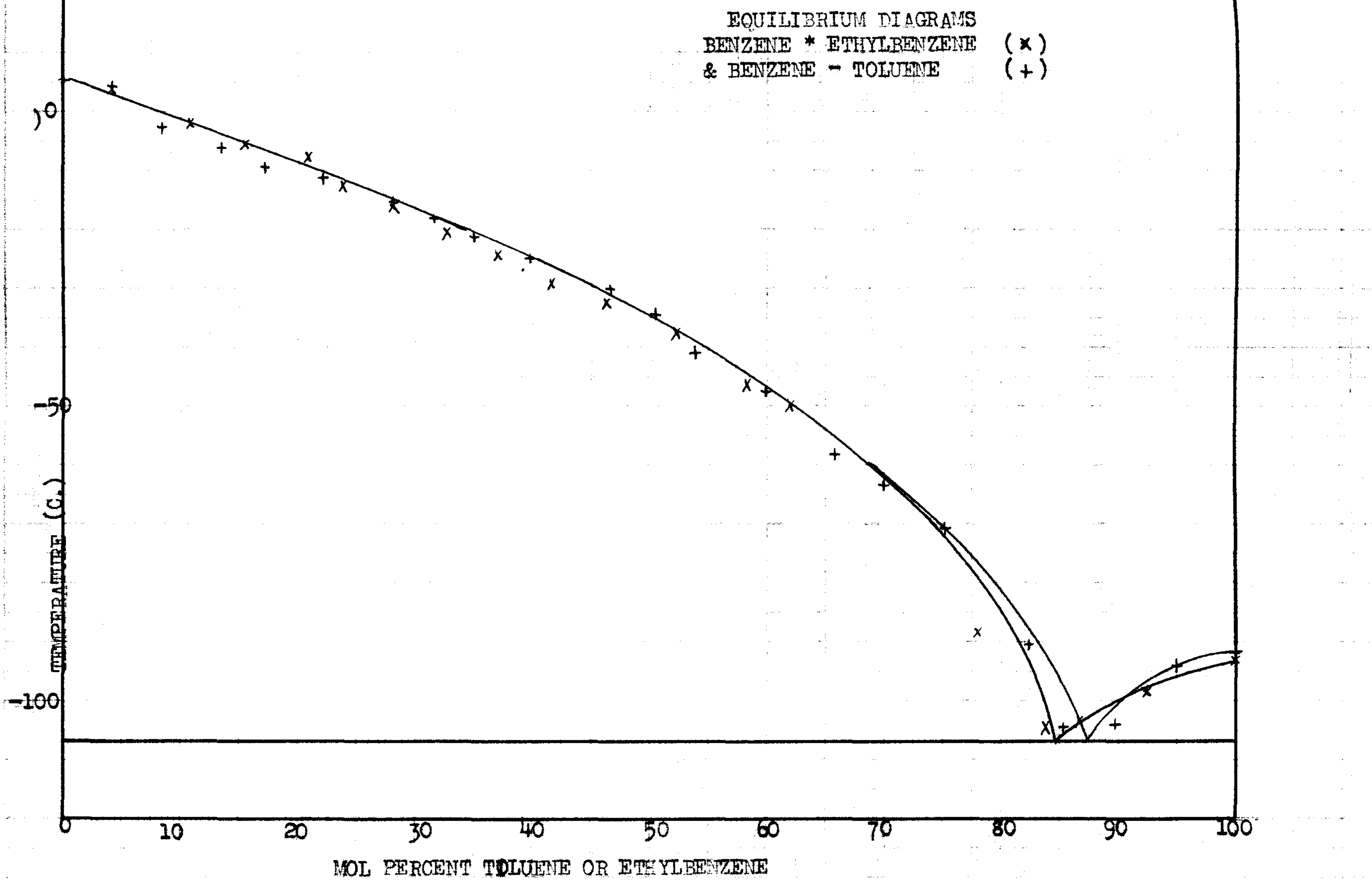
TABLE VI - 2

COMPOSITIONS AND EQUILIBRIUM POINTS OF MIXTURES, BENZENE-ETHYLBENZENE SYSTEM

Sample	Percent Ethylbenzene by weight	Mol Percent Ethylbenzene	Freezing Point (°C)	Eutectic Temp. (°C)
Benzene			5.5	
E-1	5.40	4.21	4.0	
E-3	14.21	10.85	-2.0	
E-4	20.32	16.0	-5.6	
E-5	24.82	20.9	-7.7	
E-6	29.80	23.8	-12.3	
E-7	34.74	28.2	-16.0	
E-8	39.76	32.7	-20.3	
E-9	44.02	37.0	-24.2	
E-10	49.13	41.6	-29.2	
E-11	54.21	46.4	-32.7	
E-12	59.99	52.3	-37.5	
E-13	65.62	58.4	-46.5	
E-14	69.00	62.0	-50.0	
E-20	82.73	78.0	-88.5	-107.6
E-21	87.13	83.8	-104.4	-106.0
E-22	89.86	86.7	-103.5	-107.8
E-17	90.25	87.3	-	-107.3
E-19	94.38	92.5	-98.5	-104.5
Ethylbenzene	100.00	100.00	-92.8	


EQUILIBRIUM DIAGRAM
BENZENE - ETHYLBENZENE SYSTEM
0
-50
-100
TEMPERATURE (°C.)
SOLID BENZENE
+ LIQUID
LIQUID
LIQ.
+
E.B.
SOLID BENZENE + ETHYLBENZENE
0
10
20
30
40
50
60
70
80
90
100
COMPOSITION: PERCENT ETHYLBENZENE


EQUILBRIUM DIAGRAMS
BENZENE - ETHYLBENZENE (x)
& BENZENE - TOLUENE (+)
0
-50
-100
TEMPERATURE (°C.)
0
10
20
30
40
50
60
70
80
90
100
PERCENT TOLUENE OR ETHYLBENZENE BY WEIGHT



EQUILIBRIUM DIAGRAMS
BENZENE * ETHYLBENZENE (x)
& BENZENE - TOLUENE (+)
TEMPERATURE (C.)
0
-50
-100
0
10
20
30
40
50
60
70
80
90
100
MOL PERCENT TOLUENE OR ETHYLBENZENE

RECOMMENDATIONS FOR FUTURE WORK

I. Future investigations should be carried out to complement the present study of phase diagrams of binary systems of benzene and mono-substituted benzenes.

II. The data from this series of investigations should be correlated, to determine what relation, if any, exists between the shape of the equilibrium diagram and the nature of the substituent group.

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The thesis, "A Study of the Equilibrium Diagrams of the Systems, Benzene-Toluene and Benzene-Ethylbenzene", written by John B. Mullen, has been accepted by the Graduate School with reference to form, and by the readers whose names appear below, with reference to content. It is, therefore, accepted in partial fulfillment of the requirements for the degree of Master of Science.

Dr. Parent	June 1, 1940
Dr. Schmeing	June 4, 1940